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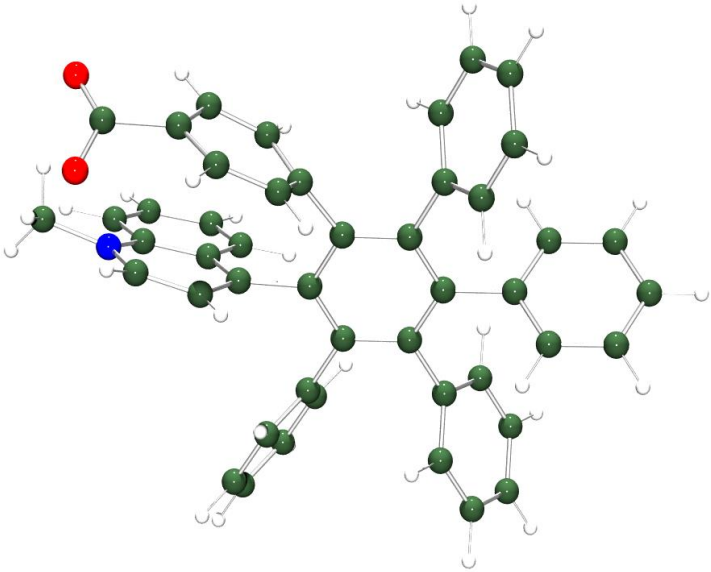
π-Extended Quinolinium Derivatives: Synthesis, Properties, Classification

Sviatoslav Batsyts



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π-Extended Quinolinium Derivatives: Synthesis, Properties, Classification

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S. Batsyts, F. J. Ramírez, J. Casado, J. C. Namyslo, A. Schmidt*. Chemistry and spectroscopy of cross-conjugated and pseudo-cross-conjugated quinolinium-ethynyl-benzoate mesomeric betaines. *Z. Naturforsch. B* **2018**, *73*, 481-491.

A. Schmidt*, **S. Batsyts**, A. Smeyanov, T. Freese, E. G. Hübner, M. Nieger. Dipolar Bent and Linear Acetylenes Substituted by Cationic Quinolinium and Anionic Benzoates. Formation of Mesomeric Betaines. *J. Org. Chem.* **2016**, *81*, 4202-4209.

Якби ви вчились так, як треба,
то й мудрость би була своя.

Т. Г. Шевченко

А хто з приятеля перекинувся в ворога, той, значить, і раніше не був приятелем і не буде.

І. Я. Франко

List of Abbreviations

abs	absolute
Ad	1-adamantyl
AH	alternant hydrocarbon
br	broad
°C	temperature in degrees Celcius
CCMB	cross-conjugated mesomeric betaine
CD_3OD	deuterated methanol
CMB	conjugated mesomeric betaine
DCM	dichloromethane
DFT	density functional theory
Dip	2,6-diisopropylphenyl
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EE	ethyl acetate
equiv	equivalent
Et	ethyl
h	hour (hours)
^{1}H NMR	proton nuclear magnetic resonance spectroscopy
HMB	heterocyclic mesomeric betaines
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry

Hz	hertz
IR	infrared spectroscopy
IR (ATR)	infrared spectroscopy (attenuated total reflectance)
J	coupling constant
LiHMDS	lithium *bis*(trimethylsilyl)amide
LUMO	lowest unoccupied molecular orbital
m	multiplet
MB	mesomeric betaine
Me	methyl
MEBYNOL	2-methyl-3-butyn-2-ol
Mp	melting point
MS (ESI)	mass spectroscopy (electrospray ionization)
n	normal
NEt_3	triethylamine
NHC	N-heterocyclic carbene
Osc. str.	oscillator strength
PCCMB	pseudo-cross-conjugated mesomeric betaine
PE	petroleum ether
Ph	phenyl
ppm	parts per million
RSA	retrosynthetic analysis
rt	room temperature

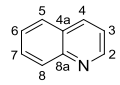
TDDFT	time-dependent density functional theory
TfO	triflate
TLC	thin-layer chromatography
TM	target molecule
THF	tetrahydrofuran
UV/Vis	ultraviolet/visible spectroscopy

Table of Contents

1. INTRODUCTION

1.1 Quinoline

Quinoline[1] **1** is a heterocyclic aromatic organic compound. It has a bicyclic structure, consisting of a six-membered benzene ring fused to a six-membered nitrogen-containing pyridine ring (Scheme 1).



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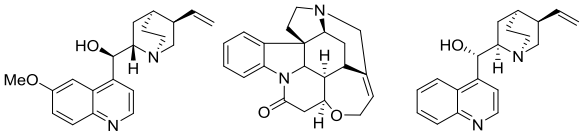
Scheme 1: Quinoline **1**

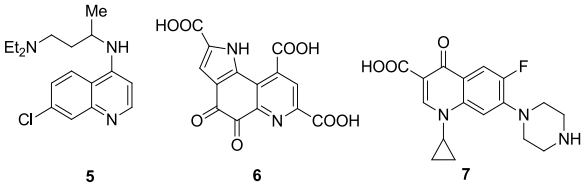
Quinoline was first extracted in 1834 from coal tar[2]. The quinoline nucleus occurs in several natural compounds such as Cinchona Alkaloids. In 1842 quinoline was obtained[2] by dry distillation of quinine **2**, strychnine **3**, or cinchonine **4** with potassium hydroxide (Scheme 2).



2 **3** **4**

Scheme 2: Alkaloids used for the first synthesis of quinoline

Derivatives of quinoline display a broad range of biological activities[3]. Thus, quinoline derivatives have been found to possess anti-bacterial[4], antimalarial[5], antifungal[6], anthelmintic[7], antiviral[8], anticonvulsant, cardiotonic, anti-inflammatory,[9] and analgesic[10] activities. A few other compounds with a quinoline ring system such as chloroquine **5** (medication), pyrroloquinoline quinone **6** (redox cofactor), and ciprofloxacin **7** (antibiotic) are given in Scheme 3.

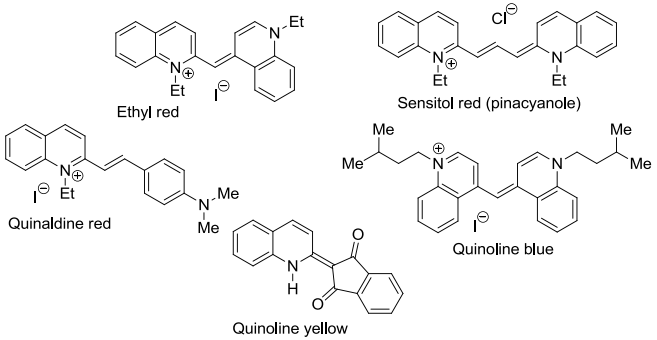


5 6 7

Scheme 3: Compounds with quinoline ring system

Quinoline derivatives are also used in polymer chemistry[11], optoelectronics, organic electronics,[12] as precursors to obtain organic light-emitting diodes, and in solar cells[13].

Quinolinium salts were also used as first sensitizing dyes[14] (Scheme 4). Quinoline yellow (solvent yellow 33)[15] is applied in the yellow colored smoke formulation. Quinoline yellow WS (with sulfonate groups) is employed as a greenish yellow food additive (E104)[16] in certain countries.



Scheme 4: Examples of quinolinium salts

The chemical properties of quinoline are similar to pyridine. Quinoline is an electron-poor aromatic compound. The greater electronegativity of the nitrogen atom decreases the electron density *(-I* effect) of the ring, thereby deactivating it. As a result, the benzene ring has the higher electron density. Hence, electrophilic substitution can take place preferentially on it. Likely, electrophilic substitution of the quinoline ring can be compared to 1-nitronaphthalene. The electrophilic substitution, such as nitration[17] and bromination[18], was observed at position 5 and 8 of the quinoline ring. In the case of

sulfonation[19], the main product is an 8-substituted quinoline. Nevertheless, thermodynamic reaction control (250 °C) leads to the formation of a 6-substituted quinoline instead of the 5-substituted isomer (kinetic control). The presence of the electron-withdrawing nitrogen atom activates the pyridine ring in quinoline towards nucleophilic substitution in electron-deficient positions 2[20] and 4[21].

1.2 Heterocyclic mesomeric betaines

Betaines are neutral compounds which can be exclusively written by dipolar structures. Heterocyclic mesomeric betaines (HMBs) are unsaturated heterocyclic compounds in which positive and negative charges are involved in conjugation. The first known HMB **8** was synthesized by FISCHER and BESTHORN in 1882. However, the structure of this compound (**8B**) was not elucidated before 1969[22] (Scheme 5).

8A **8B**

Scheme 5: First HMB (**8**) prepared by FISCHER and BESTHORN

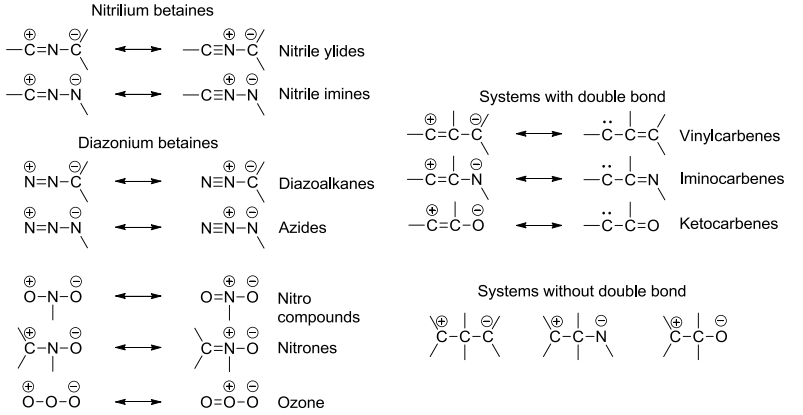
According to the classification of HMBs by RAMSDEN, OLLIS, and STANFORTH[23] in 1985 using *the valence bond approach*, the difference between conjugated, cross-conjugated and pseudo-cross-conjugated mesomeric betaines is based on the following three rules:

Rule 1 "*Conjugated mesomeric betaines are associated with dipolar canonical forms which include (i) electron octet structures and (ii) electron sextet structures with internal octet stabilisation but exclude (iii) electron sextet structures without internal octet stabilisation. The dipolar canonical forms do provide common sites for formal positive and negative charges."*

Rule 2 "*Cross-conjugated mesomeric betaines are associated with dipolar canonical forms which include (i) electron octet structures and (ii) electron sextet structures with internal octet stabilisation but exclude (iii) electron sextet structures without internal octet stabilisation. The dipolar canonical forms do not provide any common sites for formal positive and negative charges."*

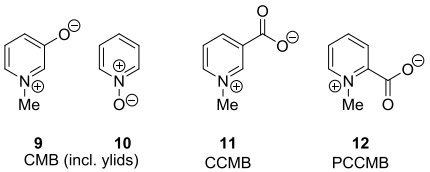
Rule 3 "*Pseudo-cross-conjugated mesomeric betaines are associated with dipolar canonical forms which include (i) electron octet structures, (ii) electron sextet structures with internal octet stabilisation and (iii) electron sextet structures without internal octet stabilisation. The dipolar canonical forms do provide common sites for formal positive and negative charges.*"

As a basis for these rules, RAMSDEN used the classification of 1,3-dipoles by HUISGEN[24,25] (Scheme 6).



Scheme 6: Classification of 1,3-dipoles with electron sextet structures with internal octet stabilization (left column), and without (right column) by HUISGEN

Examples belonging to the three different classes of pyridinium betaines are given in Scheme 7:

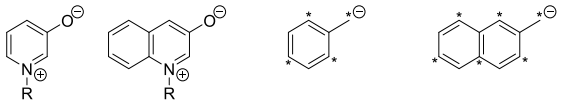


Scheme 7: Representatives of the three classes of mesomeric betaines according to the classification of 1985

Other methods to identify CMBs, CCMBs, and PCCMBs proposed by RAMSDEN[23] are *the identification of characteristic dipole moments* and *the perturbation molecular orbital approach*.

According to *the perturbation molecular orbital approach*, two additional rules were added:

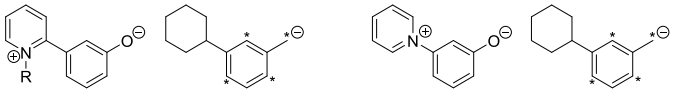
Rule 4 "*For conjugated heterocyclic mesomeric betaines which are isoconjugate with odd alternant hydrocarbon anions, the heteroatom which contributes two electrons to the total π-electron system must be located at one of the unstarred positions of the isoconjugate odd alternant hydrocarbon anion* (Scheme 8)."



9 13

Scheme 8: Illustration of "Rule 4" for the determination of CMBs

Rule 5 "*If (i) the delocalised negative charge of the heterocyclic mesomeric betaine is associated with a fragment which is isoconjugate with an odd alternant hydrocarbon anion, (ii) this fragment is connected through its unstarred positions to the remainder of the π-electron system of the molecule, and (iii) this fragment does not contain the heteroatom accommodating the positive charge, then the heterocyclic mesomeric betaine is either cross-conjugated or pseudo-cross-conjugated* (Scheme 9)."

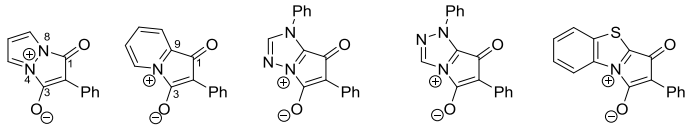


14 15

Scheme 9: Illustration of "Rule 5" for the determination of PCCMBs and CMBs

In addition, each class of MBs[23] is divided into four subclasses where betaines are isoconjugated with: (i) odd alternant hydrocarbon anions, (ii) odd non-alternant hydrocarbon anions, (iii) even alternant hydrocarbon anions, and (iv) even non-alternant hydrocarbon anions. As a result, the authors defined 12, or considering CMBs such as *N*-ylides as one additional class, 16 different types of HMBs in total. In addition, the classification was considered as comprehensive.

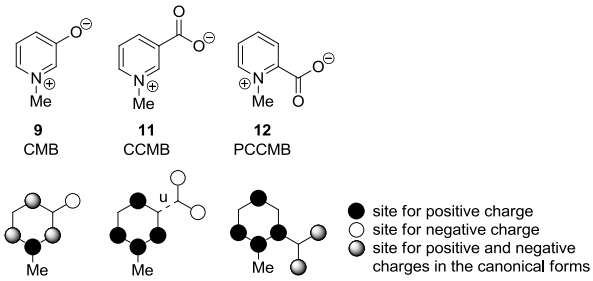
It is worth mentioning that POTTS[26] reported on the synthesis of some CCMBs and PCCMBs in 1988 (Scheme 10) and figured out that (i) PCCMBs are not always stable, and (ii) ergo there is no difference between PCCMBs and CCMBs[27] in X-ray data, the chemical behavior and dipole moments of CCMB **16** and PCCMB **17**.



Scheme 10: CCMB **16** and PCCMBs **17**-**20** synthesized by POTTS (1988)

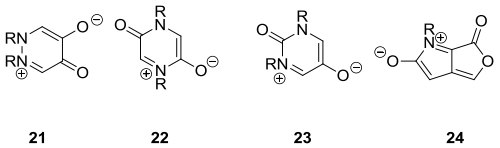
The bond lengths C1-C9, and C3-N of betaine **17** are 151.0(3), and 151.6(3) pm and are comparable to the bond length of C1-N8 (149 pm) in **16**, which is a "union bond", and corresponds to a normal C-N single bond.

The alkaloid *Trigonelline* (**11**, 1885[28]) as well as the alkaloid *Homarine* (**12**, 1933[29]) are examples of natural betaines. They belong to the classes of CCMB and PCCMB, respectively (Scheme 11). However, they behave differently when heated: *Homarine* decarboxylates[29] in aprotic non-polar solvents at rt, similar to other PCCMBs[30]. In contrast, *Trigonelline* decarboxylates at a temperature higher than 100 °C which leads to decomposition[31]. In addition, decarboxylation of *N*-methylpyridinium-2,3-dicarboxylate extrudes CO_2 easily from the C2 carbon atom[32] (the pseudo-cross-conjugated position). PCCMBs have been considered as hybrids between CMBs and CCMBs: as the charges are effectively, but not exclusively, delocalized in separated parts of the common π-electron system in PCCMBs[33] the term "pseudo-cross-conjugated" mesomeric betaines[23] was proposed. Nowadays, MBs are presented using charge distribution according to their mesomeric structures[33,34] (Scheme 11) which also have good correlations with their HOMO/LUMO profiles[33–35].



Scheme 11: Examples of the three main classes of betaines, and charge distribution according to their mesomeric structures

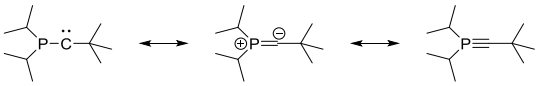
Furthermore, the classification of HMBs was expanded by RAMSDEN in 2013[36] by the inclusion of betaines isoconjugated with hydrocarbon dianions, and two more classes were added, semi-conjugated, and pseudo-semi-conjugated heterocyclic mesomeric betaines (Scheme 12). This is based on a so-called connectivity-matrix analysis and gives seven possible connectivity matrices by which five classes of HMBs have been identified.



Scheme 12: Examples of semi-conjugated (**21**, **22**), and pseudo-semi-conjugated heterocyclic mesomeric betaines (**23**, **24**) by RAMSDEN

1.3 N-Heterocyclic carbenes

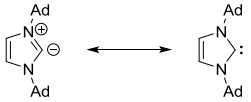
The first stable carbene **25** was obtained by BERTRAND et al. in 1988[37]. A strong multiple-bond character stabilizes **25** but nonetheless, it can react as a carbene species (Scheme 13).



25

Scheme 13: First stable carbene **25** according to BERTRAND

Three years later, the N-heterocyclic carbene **26** was synthesized by ARDUENGO et al.[38] *via* deprotonation of 1,3-di-1-adamantylimidazolium chloride with sodium hydride (Scheme 14).



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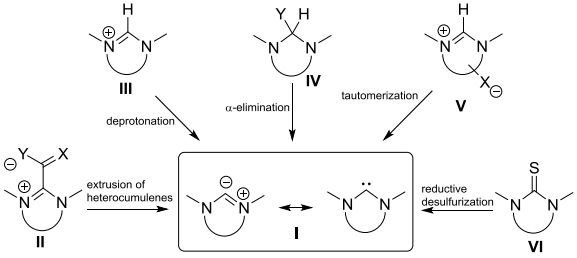
Scheme 14: First N-heterocyclic carbene **26** synthesized by ARDUENGO

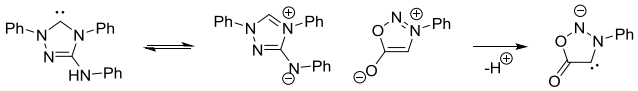
Nowadays[39], several preparative ways to obtain NHCs **I** from cyclic precursors such as heterocumulenes **II**, hetarenium salts **III**, partially saturated systems **IV**, MBs **V**, and thiones **VI** are known (Scheme 15).



Scheme 15: Preparative routes to synthesis of NHCs **I** from cyclic precursors

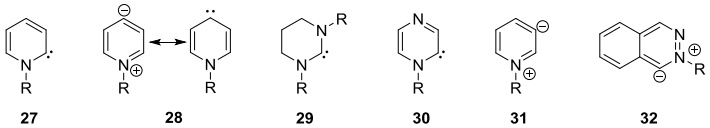
The generation of N-heterocyclic carbenes from mesomeric betaines[40] or of their anionic derivatives[41], formed by deprotonation[42] or tautomerization[43] has been recognized and applied as starting materials very recently.

The chemistry of MBs translates into the chemistry of N-heterocyclic carbenes[40,44,45]. Some examples[45] are given in Scheme 16:



Scheme 16: Relation between MBs and NHCs

In comparison to five-membered NHCs, the chemistry of six-membered NHCs is less explored. In 1937, pyridin-2-ylidene **27** was proposed as a reactive intermediate of the Hammick reaction[46] and later identified by mass spectroscopy combined with computational quantum chemistry[47] (Scheme 17).



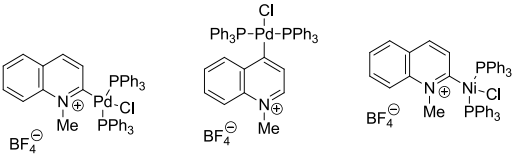
Scheme 17: Six-membered N-heterocyclic carbenes

Palladium complexes of pyridin-2-ylidene **27** (R=H) and pyridin-4-ylidene **28** (R=H) as well as of their quinoline derivatives were prepared starting from the corresponding chlorohetarenium salts by oxidative addition of $Pd(PPh_3)_4$ and, furthermore, they were screened for their catalytic activities[48]. Other transition metal complexes such as nickel[49], osmium[50], and iridium[51] are known. Trapping reactions have been performed[52]. Pyridin-4-ylidene **28** is a remote NHC and can be represented by an electron sextet structure similar to normal NHCs, whereas pyridin-3-ylidene, another remote NHC, can only be presented by dipolar structure **31**.

Carbene **29** has been reported as stable *N,N'*-diamidocarbene[53] and its reactivity was examined in detail[54].

The pyrazin-2-ylidene **30** was formed by decarboxylation of its PCCMB precursor[55], but merely its mass spectrometric examinations are available[56]. The six-membered heterocycle phthalazine can form a carbene complex with palladium by insertion into chlorophthalazine which enables the formation of phthalazine derivatives of **32**[57], among those phthalazinylidenes[58].

Stable quinolinium carbenes are not known, and only a few carbene complexes have been synthesized so far[48,59]. Some examples are given in Scheme 18:



Scheme 18: Quinolinium carbene complexes

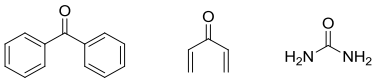
1.4 Conjugation

For a full understanding of the character of compounds such as salts, HMBs, or NHCs and in order to find an appropriate formulation of their structures, the rules of resonance are an invaluable source. They are a useful tool whenever unsaturated compounds are dealt with.

The rules of resonance[60]:

1. *All the canonical forms must be bona fide Lewis structures.*
2. *The positions of the nuclei must be the same in all the structures.*
3. *All atoms taking part in the resonance, that is, covered by delocalized electrons, must lie in a plane or nearly so. This, of course, does not apply to atoms that have the same bonding in all the canonical forms. The reason for planarity is a maximum overlap of the* π *orbitals.*
4. *All canonical forms must have the same number of unpaired electrons.*
5. *The energy of the actual molecule is lower than that of any form, obviously.*
6. *All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most.*
a. *Structures with more covalent bonds are ordinarily more stable than those with fewer.*
b. *Stability is decreased by an increase in charge separation. Structures with formal charges are less stable than uncharged structures. Structures with more than two formal charges usually contribute very little. An especially unfavorable type of structure is one with two like charges on adjacent atoms.*
c. *Structures that carry a negative charge on a more electronegative atom are more stable than those in which the charge is on a less electronegative atom.*
d. *Structures with distorted bond angles or lengths are unstable.*

In addition, cross-conjugation[61] is a peculiar type of conjugation. Classical examples of cross-conjugation are present in benzophenone or divinylketones (Scheme 19). The phenyl rings in benzophenone are conjugated with the carbonyl group, but not with each other.

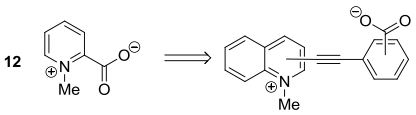


Scheme 19: Compounds with cross-conjugation

2. MOTIVATION

Heterocyclic mesomeric betaines are defined as neutral conjugated molecules which can be represented exclusively by dipolar structures in which an even number of positive and negative charges are delocalized within the π-electron system.

After the last classification (2013), HMBs can be divided into five classes, and nine sub-classes based on connectivity-matrix analyses. In order to prove the translation of the classification into the chemistry of mesomeric betaines, more detailed experimental and spectroscopic studies are necessary. The insertion of functional groups or modifications of the main skeleton of HMBs can open new opportunities and applications of these classes of compounds.



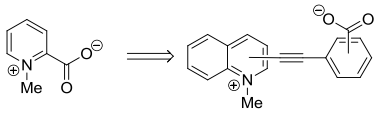
Scheme 20: π-Extended betaines

Here, we want to present syntheses and properties of quinoline-based MBs and related compounds, including DFT calculations, with extended π-electron systems.

3. RESULTS AND DISCUSSION

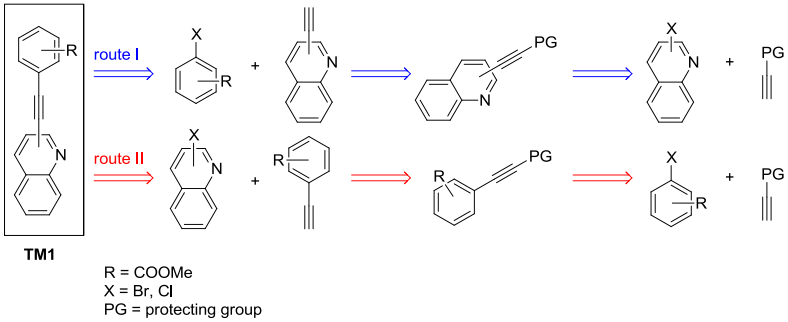
3.1 π-Extended quinolinium betaines

In this chapter, the synthesis of π-extended quinolinium betaines is described (Scheme 21).



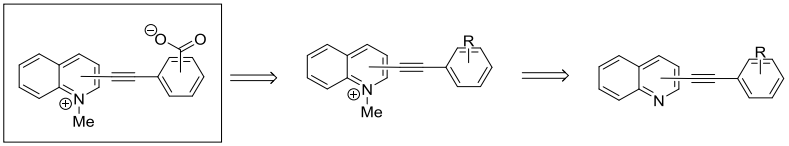
Scheme 21: Elongation of MBs

In analogy to MB **12**, the following retrosynthetic analysis (RSA) was proposed to yield the π-extended systems **TM1** in which the quinoline moieties were first linked *via* a phenylacetylenic spacer with a carboxylic group (Scheme 22). Quinolines were used as pyridine analogs to observe additional delocalization of charges across larger π-conjugated systems. Furthermore, the phenylacetylenic spacer was used to further extend the π-electron system. The use of acetylenic moieties possibly prevents the repulsion of hydrogen atoms between biphenyl systems.



Scheme 22: Retrosynthetic analysis (RSA) of non-symmetric internal acetylenes

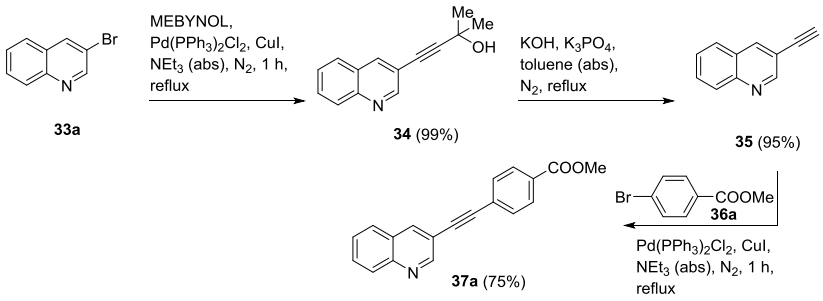
Based on the RSA, the target molecule structure **TM1** might be synthesized *via* two routes. In a first step, either haloquinolines or aryl halides can be used to synthesize protected alkynes. After deprotection, terminal alkynes might be used in a second coupling reaction with haloquinolines or aryl halides to yield the desired target molecules. Successive N-methylation of target structure **TM1** might yield cationic salts, which upon saponification might lead to the desired betaine structures **TM2** (Scheme 23).



Scheme 23: Preparation of betaines starting from neutral **TM1**

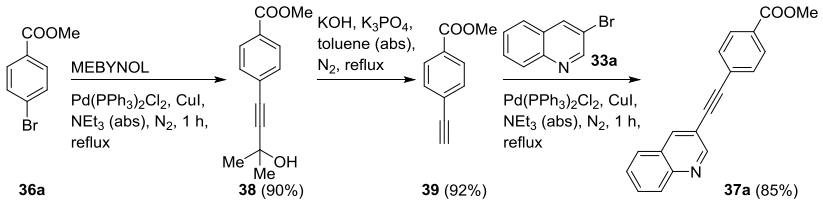
3.1.1 Synthesis of π-extended quinolines

First, the Sonogashira-Hagihara coupling reaction was used to synthesize internal acetylenes containing quinoline and substituted phenyl residues as explained in the RSA. Therefore, 3-bromoquinoline **33a**, methyl 4-bromobenzoate **36a**, and MEBYNOL were used as starting compounds. Following synthetic route I (Scheme 24), **33a** was reacted with MEBYNOL under classical Sonogashira-Hagihara conditions to give 2-methyl-4-(quinolin-3-yl)but-3-yn-2-ol **34** in almost quantitative yields. Subsequent deprotection of **34** gave 3-ethynylquinoline **35** in 95% yield. Methyl 4-bromobenzoate **36a** was then subjected to a Sonogashira-Hagihara coupling with a slight excess (1.05 equiv) of 3-ethynylquinoline **35** to give methyl 4-(quinolin-3-ylethynyl)benzoate **37a** in 75% yield.



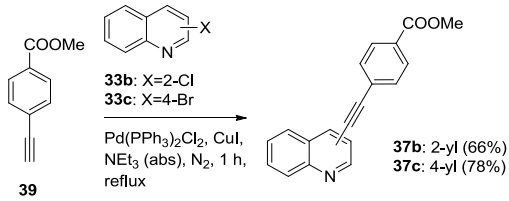
Scheme 24: Synthesis of methyl 4-(quinolin-3-ylethynyl)benzoate **37a** *via* route I

Via route II, methyl 4-ethynylbenzoate **39** was prepared in 92% yield starting from methyl 4-bromobenzoate **36a** and MEBYNOL (Scheme 25). Afterward, the second Sonogashira reaction with 3-bromoquinoline **33a** gave methyl 4-(quinolin-3-ylethynyl)benzoate **37a** in 85% yield, respectively.



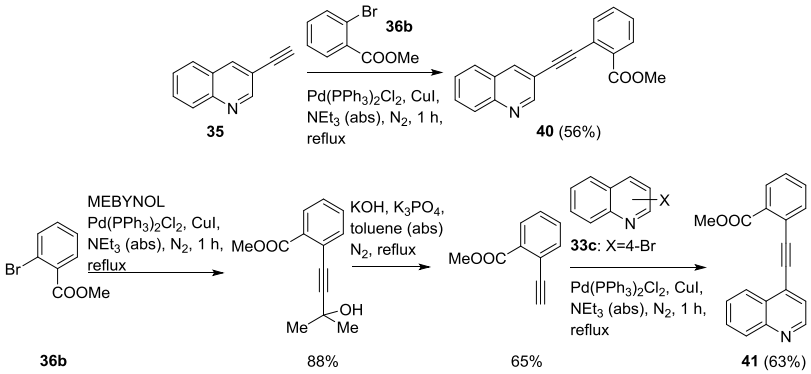
Scheme 25: Synthesis of methyl 4-(quinolin-3-ylethynyl)benzoate **37a** *via* route II

In summary, quinoline **37a** was synthesized successfully *via* routes I and II. Nevertheless, the deprotection of **38** is very sensitive to the reaction conditions: in case of insufficient reaction time, the reaction is incomplete and increasing amounts of saponification products are formed. Thus, route I proved to be more convenient in regard to synthesizing **37a**. In contrast, the reaction of 2- and 4-haloquinolines **33b**, **c** with MEBYNOL *via* route I were unsuccessful. However, the desired quinolines **37b**, **c** were prepared successfully *via* route II (Scheme 26).



Scheme 26: Synthesis of methyl 2- and 4-(quinolin-3-ylethynyl)benzoate **37b**, **c** *via* route II

Additionally, methyl 2-bromobenzoate **36b** was used to synthesize the quinolines **40** and **41**. Methyl 2-(quinolin-3-ylethynyl)benzoate **40** was obtained from 3-ethynylquinoline **35** in 56% yield *via* route I, whereas methyl 2-(quinolin-4-ylethynyl)benzoate **41** was synthesized from 4-bromoquinoline **33c** in 63% yield (Scheme 27).

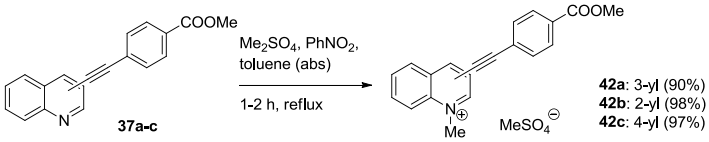


Scheme 27: Synthesis of other 3-and 4-substituted quinolines *via* route I (**40**) and II (**41**)

3.1.2 Synthesis of quinolinium salts

Upon successful synthesis of π-extended quinolines, N-methylations to quinolinium salts were performed. N-Methylation was successful with dimethyl sulfate in anhydrous toluene under reflux conditions (Scheme 28). Other methylating reagents (methyl iodide, methyl triflate) gave lower yields of quinolinium salts[35]. The obtained salts **42a-c**

proved to be insoluble in toluene and precipitated as methylsulfates in excellent yields. In the ^{1}H NMR and ^{13}C NMR spectra taken in DMSO-d_6, the methylsulfate anions gave chemical shifts in the range from 3.36 to 3.37 ppm, and from 52.7 to 52.8 ppm, respectively.



Scheme 28: Synthesis of methylquinolinium salts **42a-c**

Anion exchange reactions to hexafluorophosphate salts show that hexafluorophosphate anions provide a better solubility in acetonitrile in comparison to methylsulfate analogs **42a-c**. Hence, it was possible to obtain single crystals of **42aPF$_6$** by slow evaporation of a concentrated solution in acetonitrile in contrast to methylsulfate salt **42a**. Single crystals were analyzed by X-ray analysis, the molecular drawing of which is shown in Figure 1.

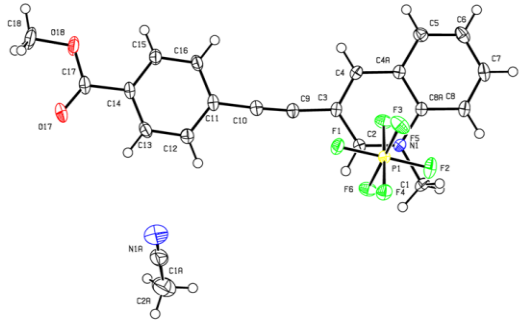
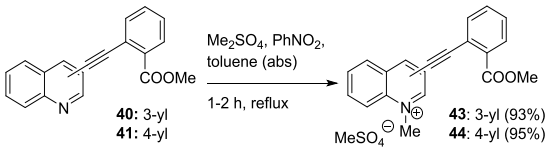


Figure 1: Crystal structure determination of **42aPF$_6$** and a single acetonitrile molecule

Salt **42aPF$_6$** crystallized monoclinic. The quinoline ring and the phenyl ring are planar with respect to each other. The dihedral angle between the phenyl ring and the

carboxylic group is only 3.3°. The C≡C triple bond is slightly bent with a deviation of 5.7° for C3-C9-C10 and 3.1° for C9-C10-C11. C3-C9 and C10-C11 are typical sp-sp^2 C-C single bonds and have bond lengths of 142.92(14) and 143.28(16) pm, respectively. The bond length between C9 and C10 is 119.56(18) pm, which corresponds to the length of the C≡C triple bond.

Furthermore, quinolines **40**, **41** were successfully methylated by dimethyl sulfate in excellent yields as well (Scheme 29).



Scheme 29: Methylation of quinolines **40**, **41**

After an anion exchange reaction to a hexafluorophosphate salt, single crystals of **43PF$_6$** were obtained as yellow plates from a concentrated hot solution in methanol (Figure 2).

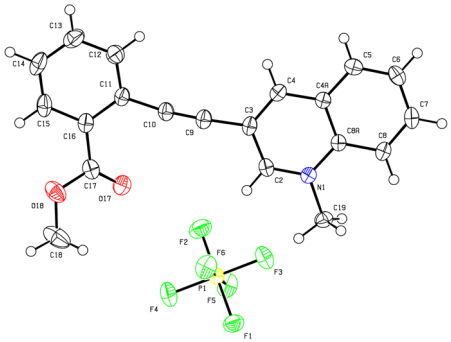


Figure 2: Crystal structure determination of **43PF$_6$**

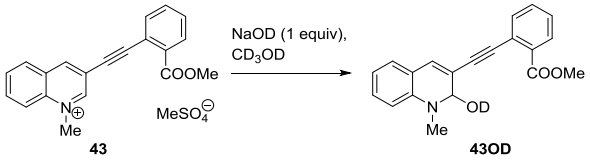
In comparison to **42aPF$_6$**, salt **43PF$_6$** crystallized monoclinic as well. Both quinoline and phenyl ring are almost planar with respect to each other. The dihedral angle

between them is just 7.1°. But unlike in the carboxylic group in the para position, the ortho-substituted carboxylic group is slightly twisted and has a dihedral angle with the phenyl ring of 25.7°, which is likely to be a consequence of the interaction between the oxygen atom of the carboxylic group and C10 carbon atom of the C≡C triple bond. This results in an increasing deviation of the C11-C10-C9 angle in the triple bond to 7.6°. The deviation of the angle of the C≡C triple bond (C3-C9-C10) is comparable to the crystal mentioned before and has a value of 3.3°. In both cases the C≡C triple bond has a cisoid conformation.

In the following segments, the quinolinium salts **43** and **42a-c** were saponified to further undergo deprotonation reactions upon treatment with adequate bases to form the desired betaines **TM2**.

3.1.3 Saponification of salt 43

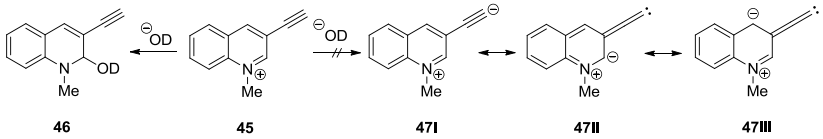
Firstly, an NMR experiment of ester **43** in CD_3OD was conducted. An equivalent of sodium deuteroxide in D_2O was added during the measurement which induced no saponification. However, upfield signals of a new compound were observed in the proton spectrum. Analysis of 2 D NMR spectra elucidated the loss of the positive charge in the quinolinium ring, explaining the upfield shift of the protons. Interestingly, compound **43OD** was formed as a result of the nucleophilic attack of the deuteroxy group to the quinolinium ring in 2-position (Scheme 30).



Scheme 30: Interaction between NaOD (1 equiv) and salt **43**

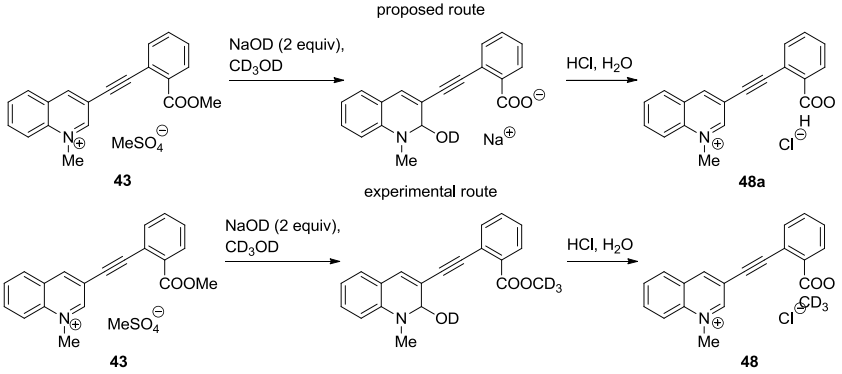
These results were used to explain the chemical shifts mentioned in the work of SMEYANOV, SCHMIDT[62] (Scheme 31). Previously, the upfield shifts of protons in

compound **45** were presented due to delocalization of negative charge in 2- and 4-positions of the quinolinium ring[62] (canonical forms **47I-III**). However, in analogy to Scheme 30, compound **46** was formed[63]. Hence, the upfield shifts of the proton signals are explained by the formation of neutral compounds compared to the precursor salts.



Scheme 31: Interaction between NaOD (1 equiv) and salt **45**

Due to previous results, an excessive amount (two equiv) of sodium deuteroxide was used to saponify salt **43** (Scheme 32). At first, the absence of the ester methyl group in the proton spectrum led to the conclusion of a successful saponification. Successively, the saponification product was treated with HCl in order to cleave off the deuteroxy group in 2-position. NMR measurements showed salt **48** with identical chemical shifts without the ester methyl group. However, the related ESI mass spectrum, surprisingly, did not match the desired compound **48a**. The value of the experimental mass is 305.1 while compound **48a** had a mass of 288.



Scheme 32: Proposed and experimental routes of interaction between NaOD (2 equiv) and salt **43**

To clarify the experimental mass and structure of salt **48**, an anion exchange reaction to a hexafluorophosphate salt **48PF$_6$** was conducted as well. The obtained salt **48PF$_6$** was precipitated using an aqueous solution of NH_4PF_6 from **48**. Single crystals of **48PF$_6$** were grown from acetonitrile. X-ray analysis shows the presence of the ester carbon (Figure 3).

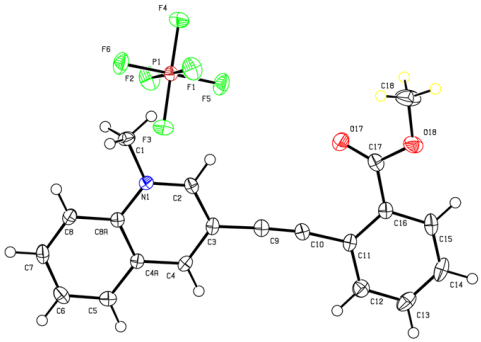
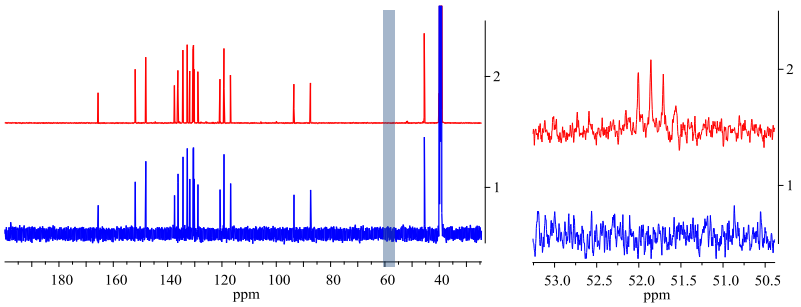


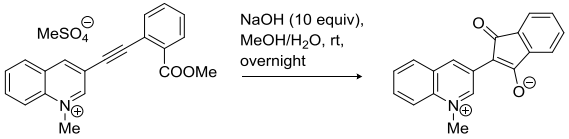
Figure 3: Crystal structure determination of **48PF$_6$**

The crystal data of **48PF$_6$** are comparable to the non-deuterated analog **43PF$_6$** with a dihedral angle between the quinoline ring and the phenyl ring of 7.5° and 25.6° between the phenyl ring and carboxylic group. This led to the conclusion that a reesterification to the deuterated methyl ester group took place, catalyzed by a second equiv of sodium deuteroxide. Additionally, long-time measurements of a ^{13}C NMR spectrum (20k scans) of **48PF$_6$** gave the multiplet signal of the deuterated carbon atom proving the crystal structure of **48PF$_6$** (Scheme 33).



Scheme 33: ^{13}C NMR spectra of compound **48PF$_6$** with 16 scans (blue spectrum) and 20k scans (red spectrum)

Since saponification did not yield the desired betaine yet, a tremendous amount (10 equiv) of sodium hydroxide was used to saponify salt **43**. In a work[34] by SMEYANOV and SCHMIDT such conditions were applied previously. Surprisingly, saponification under these conditions of **43** resulted in the precipitation of **50**. No acidification of the reaction mixture proved to be necessary (Scheme 34).



43 **50** (87%)

Scheme 34: Saponification of **43** with NaOH (10 equiv)

The difference between **43** and **50** was explained in detail *via* NMR spectroscopy in the dissertation by SMEYANOV[64], but the chemical structure of **50** remained unclear. Therefore, single crystals of **50×HCl** were grown from a saturated solution of **50** in methanol in presence of hydrochloric acid and water (Figure 4). X-ray analysis of compound **50** has proven the betaine structure as shown in Scheme 34.

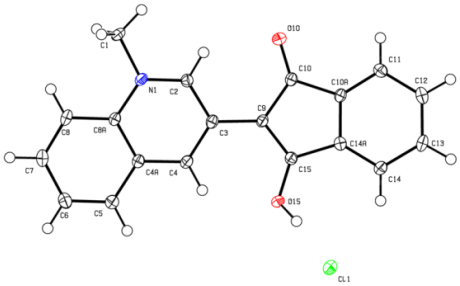
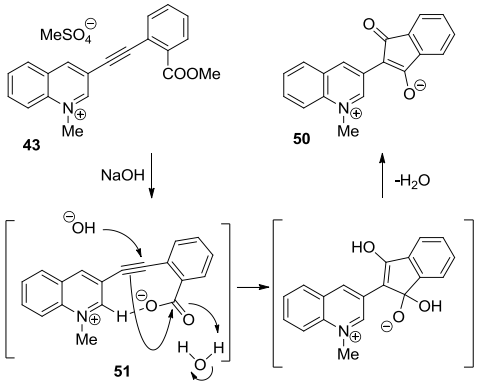


Figure 4: Crystal structure determination of **50×HCl**

According to the X-ray structure, the following reaction mechanism, as shown in Scheme 35, was proposed[35].



Scheme 35: First proposed mechanism of formation **50**

Upon treatment of salt **43** with sodium hydroxide, betaine **51** is formed first. It is assumed that betaine **51** rearranges to compound **50** due to instability caused by its molecular geometry[35].

Based on the previous insight, gained by NMR experiments of salt **43** with NaOD and crystal data of **43PF$_6$**, an alternative mechanism was proposed (Scheme 36). The dihedral angle in compound **43PF$_6$** between the carboxylic group and the phenyl ring is

25.7° (Figure 5). This indicates a 1,5 interaction between the oxygen of the carboxylic group and Cβ carbon atom of the C≡C triple bond, as the distance (285.5 pm) is considerably shorter than the sum of the van der Waals radii (O, 152 pm; C, 170 pm).

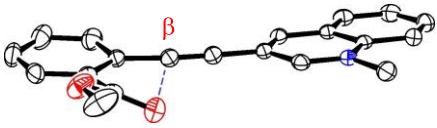
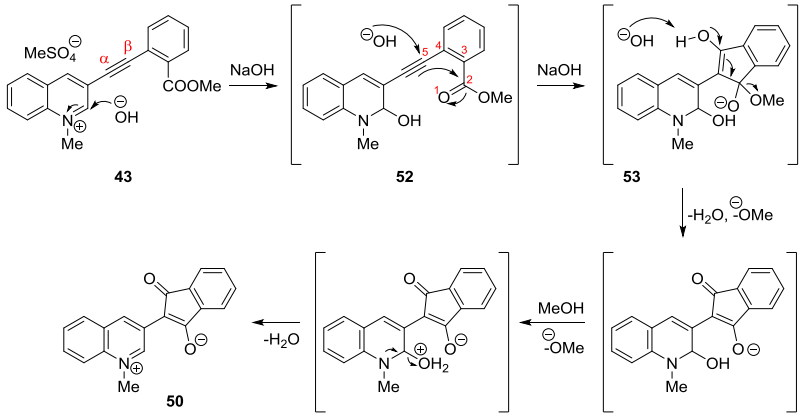


Figure 5: 1,5 Interaction between the oxygen atom and the Cβ carbon atom in the crystal structure of **43PF$_6$** (hydrogen atoms omitted for clarity)

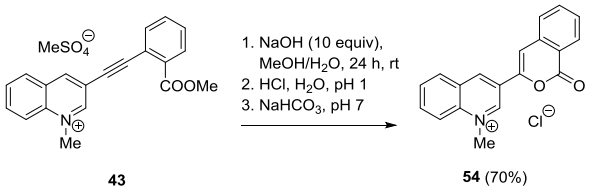


Scheme 36: Alternative mechanism for the formation of **50**

In the first step, a nucleophilic addition of a hydroxy group takes place in 2-position yielding intermediate **52**. Likely, a second nucleophilic addition of the hydroxy group to the Cβ carbon of the C≡C triple bond takes place due to a 1,5 interaction, followed by a cyclization reaction that yields intermediate **53**. Furthermore, the elimination of the methoxy group is followed by the interaction with the solvent and successive elimination of water results in **50**.

In another attempt to saponify salt **43**, a diluted methanol/water solution of sodium hydroxide was used to prevent the precipitation of **50**. The following steps were

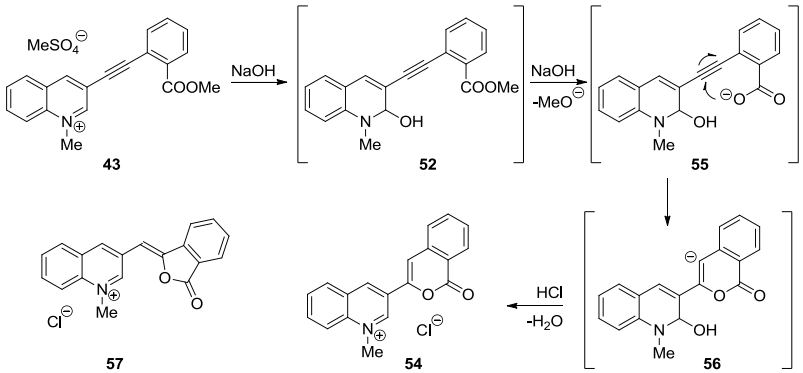
conducted in analogy to Scheme 32. Upon acidification and subsequent neutralization of the reaction mixture with sodium bicarbonate, oxoisochromene **54** was obtained in 70% yield (Scheme 37).



43 **54** (70%)

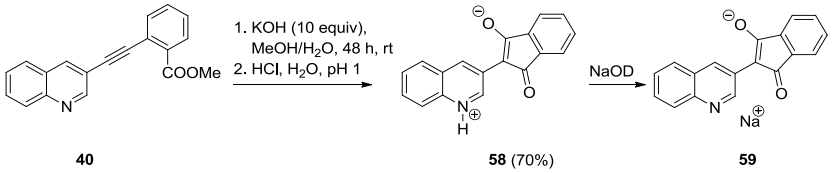
Scheme 37: Synthesis of oxoisochromene **54**

In analogy to the previous findings, the following reaction mechanism for the formation of compound **54** was proposed (Scheme 38). First, a hydroxylation of the 2-position is taking place under basic conditions. Most likely, a diluted solution of base saponifies the ester group to form intermediate **55** instead of a nucleophilic attack to the Cβ carbon of the C≡C triple bond. This might be accounted to single water molecules disturbing the 1,5-interaction by forming hydrogen bonds with the carboxylic oxygen. Afterward, a ring closing reaction takes place to a six-membered ring by the nucleophilic attack of the carboxylic anion to the Cα carbon of the C≡C triple bond to form **56**. The following acidification of the reaction mixture forces the rearomatization of the quinolinium ring to give salt **54**. As shown, the Cβ carbon of the C≡C triple bond is not activated anymore. Hence, the formation of the five-membered isomer **57** is not observed.



Scheme 38: Proposed mechanism for the formation of oxoisochromene **54**

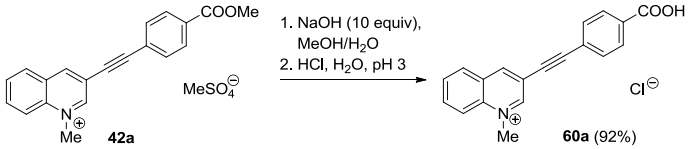
In another experiment, the saponification reaction of the neutral compound **40** was conducted prior to N-methylation in order to prevent the hydroxylation in 2-position of the quinoline residue and subsequent rearrangement reaction. Upon basic hydrolysis followed by acidification, betaine **58** precipitated as an orange solid instead. Attempts to dissolve **58** in standard solvents were unsuccessful. However, by treatment with NaOD, betaine **58** was dissolved successfully and characterized fully as sodium salt **59** *via* NMR spectroscopy (Scheme 39).



Scheme 39: Saponification of **40**

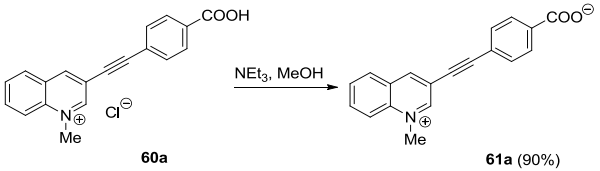
3.1.4 Saponification of the salts 42a-c

Saponification of the compounds **42a-c** was conducted under basic conditions instead of acidic ones. As previously reported, the hydrolysis with H_3PO_4, HBF_4, H_2SO_4, and HCl was not successful. However, carboxylic acid **60a**[34,35] was obtained by the reaction of ester **42a** with an excess of sodium hydroxide in a methanol/water solution, stirring overnight at rt, followed by acidification with a yield of 92% (Scheme 40).



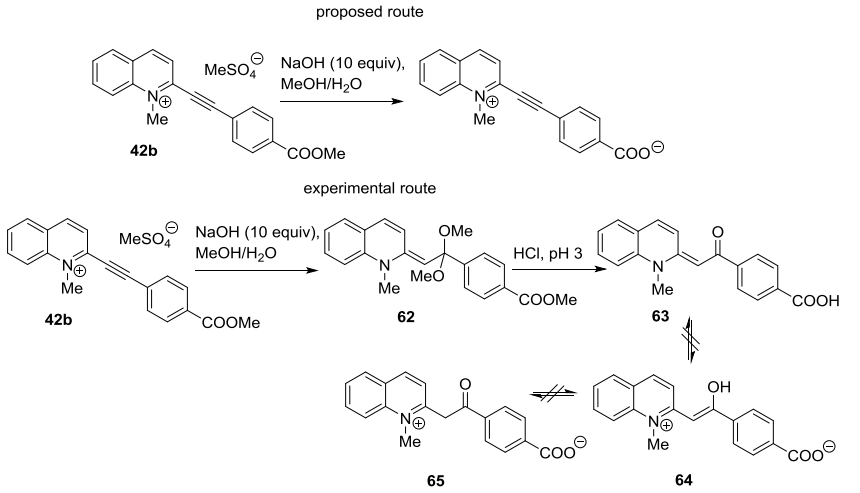
Scheme 40: Saponification of **42a**

As proven previously, hydroxylation in 2-position occurs during saponification. Thus, successive acidification is mandatory in order to release the hydroxy group. The synthesis of the carboxylic acid **60a** was proven *via* NMR spectroscopy. The carboxylic acid proton can be detected at δ = 13.31 ppm in DMSO-d_6. Using NEt_3 in methanol to deprotonate the carboxylic acid **60a**, betaine **61a** was obtained successfully (Scheme 41). Similar betaines were synthesized in the work by SMEYANOV and SCHMIDT[34].



Scheme 41: Deprotonation of **60a**

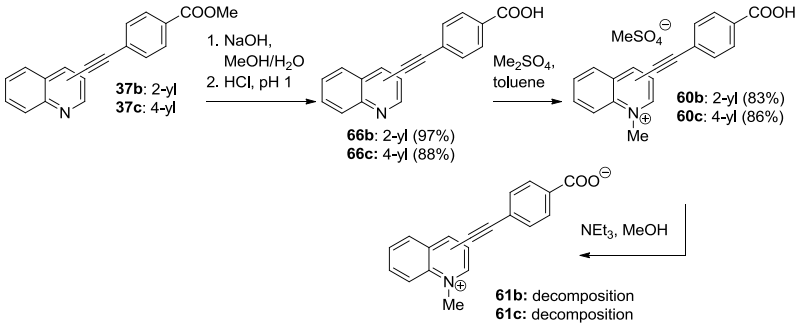
The same conditions were used for the saponification of **42b**. However, the proposed pathway did not yield the desired betaine **61b**. Instead, basic conditions led to the formation of compounds **62** and **63** due to an additional interaction with the triple bond in **42b** (Scheme 42).



Scheme 42: Saponification of **42b** and side reactions

The acetal **62** precipitated from the reaction mixture and was first filtered off (yield: 26%). Cleaning with diethyl ether let the compound unexpectedly dissolve. Via NMR the loss of the positive charge was observed due to chemical shifts of the *N*-methyl group of salt **42b** from δ = 4.79 in DMSO-d_6 to δ = 3.20 ppm in $CDCl_3$. The ester and the methoxy groups show chemical shifts of δ = 3.89 ppm and δ = 3.12 ppm, respectively. After filtration, the reaction mixture was acidified with HCl. Further work-up gave compound **63** in 70% yield. The signal of δ = 3.74 ppm is assignable to the *N*-methyl group, the value of which is between the signals of the *N*-methyl groups of the acetal **62** and the salt **42b**. The skeleton structure of **63** consists of a *β*-enaminocarbonyl chromophore. The ^{13}C NMR analysis with additional 2D NMR measurements gives resonance frequencies at δ = 184.6 ppm for the carbonyl carbon and at δ = 115.5 ppm for the exocyclic enamine carbon. Neither of the tautomers **64** and **65** is detected. The IR spectrum of **63** shows the C=O group at 1638 cm^{-1} which confirms the carboxylic acid form, whereas carboxylates give absorption peaks in the region of 1570-1580 cm^{-1}. Upon addition of DCl to the DMSO-d_6 solution of **63**, a downfield shift is observed as a result of protonation of the carbonyl oxygen.

The same method of saponification and further methylation of neutral compounds was also applied to **37b**, **c** (Scheme 43). In this reversed method (1. saponification, 2. methylation) the nucleophilic attack to the triple bond, which is activated by the additional delocalization of the positive charge onto it, is avoided.



Scheme 43: Synthesis of betaines **61b**, **c**

N-Methylation yielded the salts **60b, c** successfully. In analogy to the synthesis of **61a**, deprotonation of the salts **60b**, **c** was conducted. However, using trimethylamine the reaction did not yield the desired betaines. NMR experiments show that any basic treatment (NEt_3/DMSO-d_6; LiHMDS/MeCN-d_3, NEt_3/MeOH; proton sponge/DMSO-d_6) of compound **60c** likely leads to decomposition of the betaine **61c** (Figure 6). Upfield signals in the proton spectrum of betaine **61c** in comparison to precursor salt **60c** indicate that a betaine must have been formed (Figure 6, spectrum 2). Nevertheless, further NMR measurements show the decomposition of betaine **61c** over the period of one hour (Figure 6, spectrum 6).

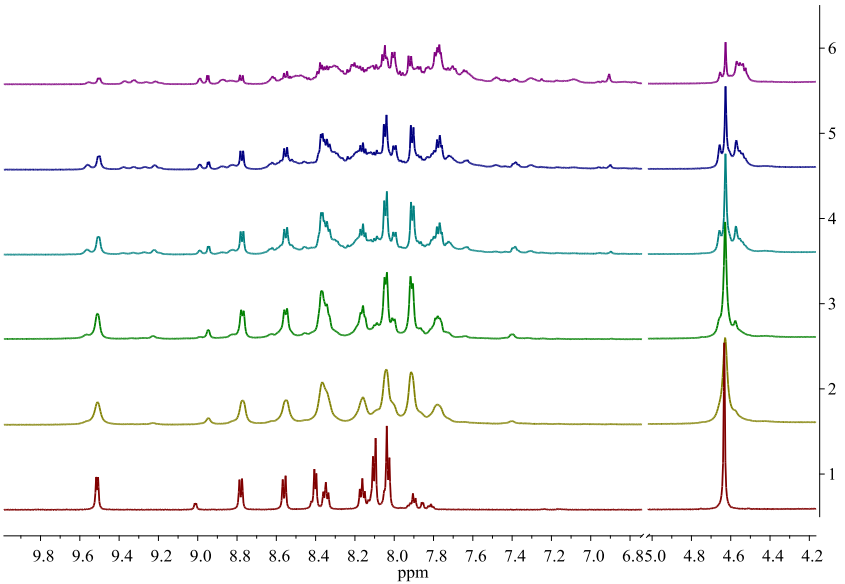
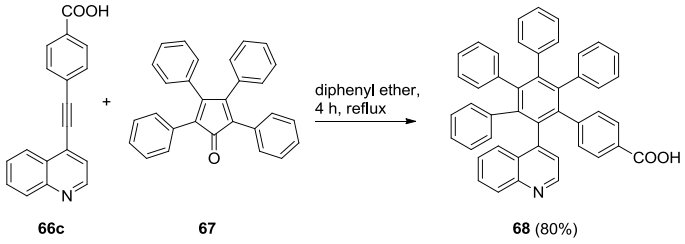


Figure 6: ^{1}H NMR spectra (600 MHz) of **60c** (Spectrum 1) and **60c**+NEt_3 (Spectra 2-6) in DMSO-d_6

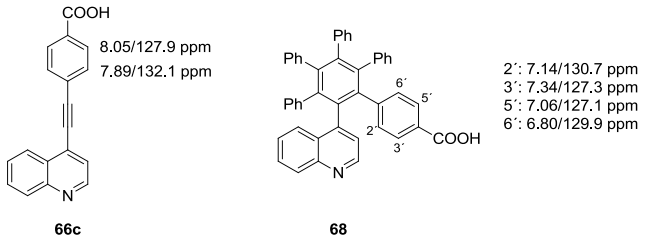
3.1.5 Synthesis of a propeller-like betaine

Due to the proven instability of the betaines **65b**, **c**, a synthetic approach to a new MBs with methylquinolinium and carboxyphenyl moieties was performed starting from **66c** under Diels-Alder conditions (Scheme 44).



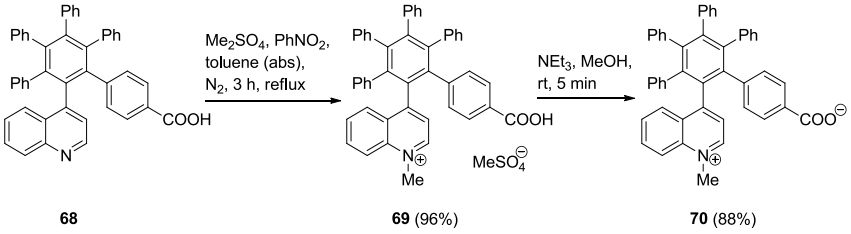
Scheme 44: Synthesis of **68**

The reaction of acetylene **66c** in diphenyl ether with cyclopentadienone **67** gave product **68** in 80% yield under reflux conditions. The propeller-like compound **68** displays interesting properties which were observed by NMR spectroscopy. In the case of **66c**, the hydrogens and appropriate carbon atoms of the phenyl ring give two different signals in the ^{1}H and in the ^{13}C NMR spectra, respectively. In contrast, the propeller-like compound **68** shows four different H/C chemical shifts in the ^{1}H and ^{13}C spectra, respectively (Scheme 45).



Scheme 45: Spectroscopic features of **68** in comparison to **66c**

Also, according to the NMR measurements, compound **68** exists only in one rotameric form in DMSO-d_6 at rt. Methylation of **68** with dimethyl sulfate is almost quantitative and gave salt **69** with 96 % yield (Scheme 46).



Scheme 46: Synthesis of propeller-like betaine **70**

In a next step, the deprotonation of salt **69** with NEt_3 was tested using NMR measurements in DMSO-d_6. According to these measurements, a deprotonation product was observed which proved to be stable in comparison to previous NMR experiments

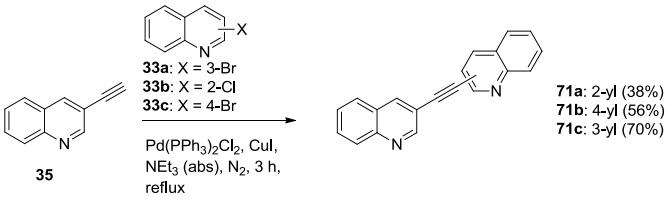
with betaine **61c**. Furthermore, in the presence of excessive amounts of base (NEt_3, 2 equiv) no changes were observed in the proton spectrum. Additional measurements after 18 h showed no changes as well. Based on the obtained results, the laboratory scale deprotonation of salt **69** in a methanolic solution with 1.3 equiv of NEt_3 gave betaine **70** with 88% yield. In addition, the total yield of **70** after seven consistent reactions, from 4-bromoquinoline **33c**, MEBYNOL, and methyl 4-bromobenzoate **36**, is 38%.

3.2 π-Extended quinolinium salts

To get a deeper view on the positive charge delocalization, dicationic compounds were synthesized and investigated.

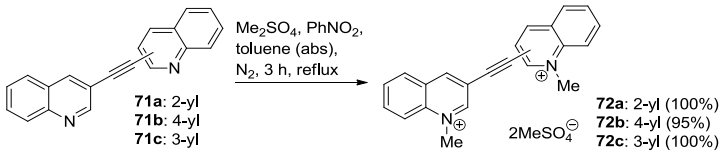
3.2.1 Synthesis of other quinolinium salts

First, 3-ethynylquinoline **35** was synthesized and successively reacted with a small excess of 2-, 3- or 4-halogenated quinoline under Sonogashira-Hagihara conditions (Scheme 47).



Scheme 47: Synthesis of conjugated diquinoline systems connected *via* an acetylenic spacer

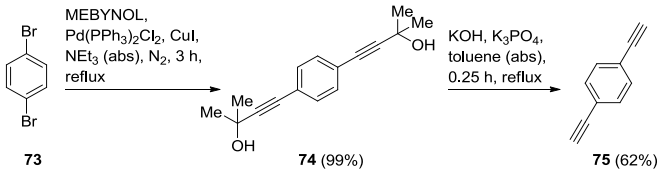
All products are solid, yellow-colored compounds which were separated by column chromatography in yields of 38% using chlorine derivative **33b**, and 56% and 70% using 4- and 3-bromo derivatives **33c**, **33a**, respectively. For the preparation of dicationic species, an excess (2.5 equiv) of dimethyl sulfate was used (Scheme 48).



Scheme 48: Methylation of diquinoline compounds **72a-c**

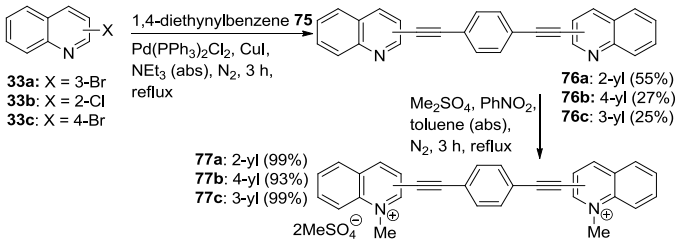
The salts **72a-c** were formed in almost quantitative yields. In addition, no monomethylated product was found in the reaction products. In comparison to the educts **71a-c**, which all have a similar color, the dimethylated salts do not: the 3,3′-derivative is a bone-colored, 3,2′- a dark violet, and 3,4′- a khaki-colored solid.

To further extend the conjugated system, 1,4-diethynylbenzene **75** was used as a new spacer. Compound **75** was synthesized in two steps from 1,4-dibrombenzene **73** and MEBYNOL with a total yield of 61% as colorless crystals (Scheme 49).



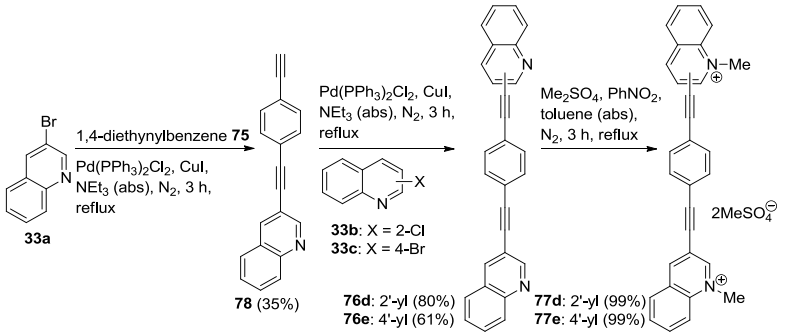
Scheme 49: Synthesis of 1,4-diethynylbenzene **75**

Subsequently, 1,4-diethynylbenzene **75** was reacted with an excess of halogenated quinolines under Sonogashira conditions as mentioned before to give new π-extended symmetric conjugated ethynyl quinolines, which were also subsequently methylated by an excess of dimethyl sulfate (Scheme 50).



Scheme 50: Synthesis of extended symmetric ethynyl quinolines **76a-c** and their salts **77a-c**

Asymmetric ethynyl quinolines were synthesized in two consistent Sonogashira reactions as well and then methylated, respectively (Scheme 51).



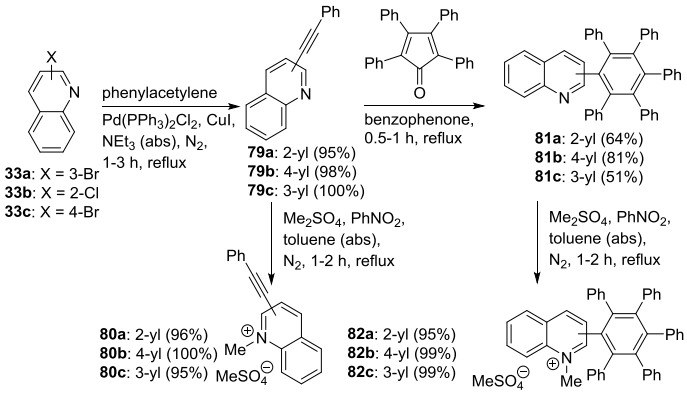
Scheme 51: Synthesis of extended asymmetric ethynyl quinolines **76d, e** and their salts

In addition, the reaction of **75** with 2-chloroquinoline **33b** or 4-bromoquinoline **33c** led to the exclusive formation of bis-coupled Sonogashira products **76a**, **b** and not of the isomers of **78** (2-yl, 4-yl).

Some of the synthesized diquinolinium dimethylsulfate salts were unstable while stored under ambient conditions for longer times. Changing the counterions to dihexafluorophosphates *via* ion exchange reactions successfully prevented this issue. Salts **72a-c** and **77a-e** were easily converted to dihexafluorophosphates analogs in almost quantitative yields.

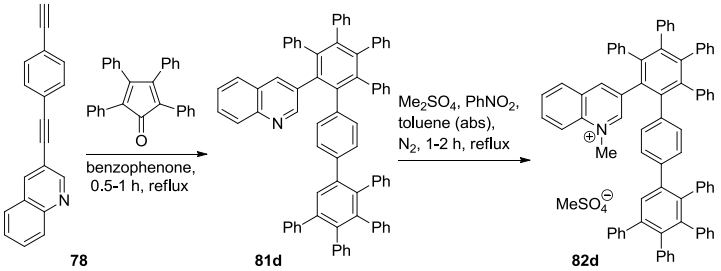
3.2.2 Synthesis of propeller-like quinolinium salts

The monocationic propeller-like compounds **82a-c** were prepared by interaction of acetylenes **79a-c** with tetraphenylcyclopentadione in benzophenone (Scheme 52) followed by successful methylation by dimethyl sulfate. Afterward, methylation of the acetylenes **79a-c**, which are the planar analogs of **81a-c**, led to the formation of salts **80a-c** with almost quantitative yields.



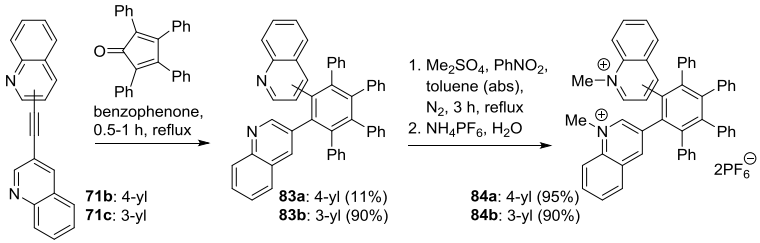
Scheme 52: Synthesis of monocationic propeller-like quinoline derivatives and planar analogs

The same conditions were tested using the diacetylenic compound **78** with an excess (3 equiv) of tetraphenylcyclopentadione to give only one reaction product, **81d** in 77% yield. Its N-methylquinolinium salts with methylsulfate (**82d**) and hexafluorophosphate anions (**82dPF$_6$**) were prepared as well (Scheme 53).



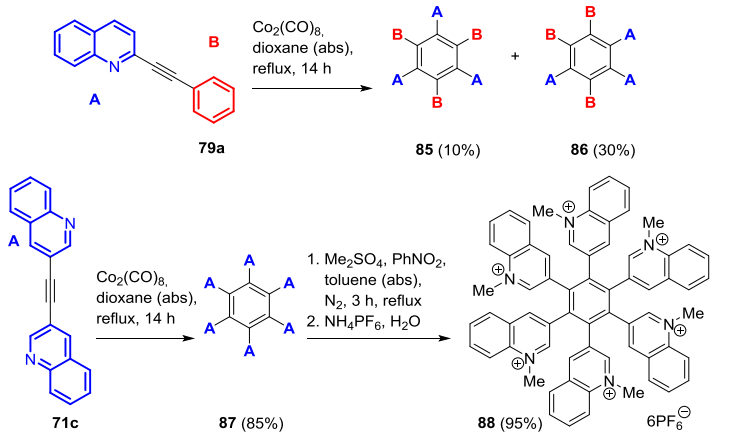
Scheme 53: Reaction of cyclopenthadione with diacetylenic compound **78**

The dicationic propeller-like quinoline compounds **83a**, **b** were prepared by a similar procedure in benzophenone under reflux conditions and used in further N-methylation reactions as well. An immediate anion exchange reaction during work-up yielded dihexafluorophosphate salts **84a**, **b** successfully (Scheme 54).



Scheme 54: Synthesis of dicationic propeller-like quinoline derivatives

The asymmetric acetylene **79a** as well as the symmetric **71c** were tested in a cobalt catalyzed trimerization reaction (Scheme 55). Trimerization of **79a** gave two isomeric products **85** and **86** with a total yield of 40%, which were successfully separated by column chromatography.



Scheme 55: Cobalt-catalyzed [2+2+2] cyclotrimerization of 2-(phenylethynyl)quinoline **89a** and 3,3'-ethyne-1,2-diyldiquinoline **82c**

In the next step, trimerization of the symmetric acetylene **71c** led to the formation of the hexasubstituted benzene **87**. Due to its chemical structure, **87** exists in eight rotameric forms. N-Methylation of **87** with an excess of dimethyl sulfate followed by precipitation with NH_4PF_6 successfully gave only one product (**88)**. However, HRMS measurements were not successful due to its polycationic (6 ×) species, whereas measuring HRMS of neutral educt **87** was not problematic. The salt **88** also exists in eight rotameric forms, which was proven by ^{1}H NMR spectroscopy (Figure 7).

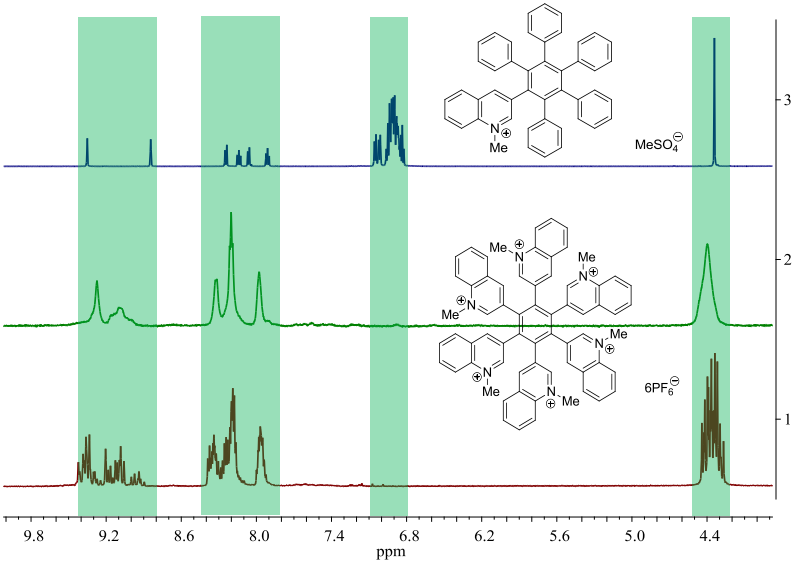


Figure 7: ^{1}H NMR spectrum of **88** at rt (1) and 100 °C (2) compared to monocationic **82c** (3)

In Figure 7 the ^{1}H NMR spectrum of compound **88** is compared to the spectrum of its monocationic analog **82c**. All proton signals are divided into four groups marked by green fields. The protons of five phenyl rings of **82c** give signals in the region from 7.1 to 6.8 ppm, whereas proton signals of the quinoline ring are shifted more downfield due to the positive charge delocalized exclusively in the quinoline system. All other proton shifts of **82c** give signals in regions which are comparable to salt **88**. Nevertheless, eight rotamers of **88** resulted in multiplet signals in its ^{1}H NMR spectrum. Salt **88** does not

have any phenyl rings (e. g., proton signals with no delocalization of the positive charge) and signals in other regions on ^{1}H NMR are not detected. This led to the conclusion that all six quinoline rings of **87** are methylated. In Figure 8 ^{1}H NMR spectra of **88** at different temperatures are presented.

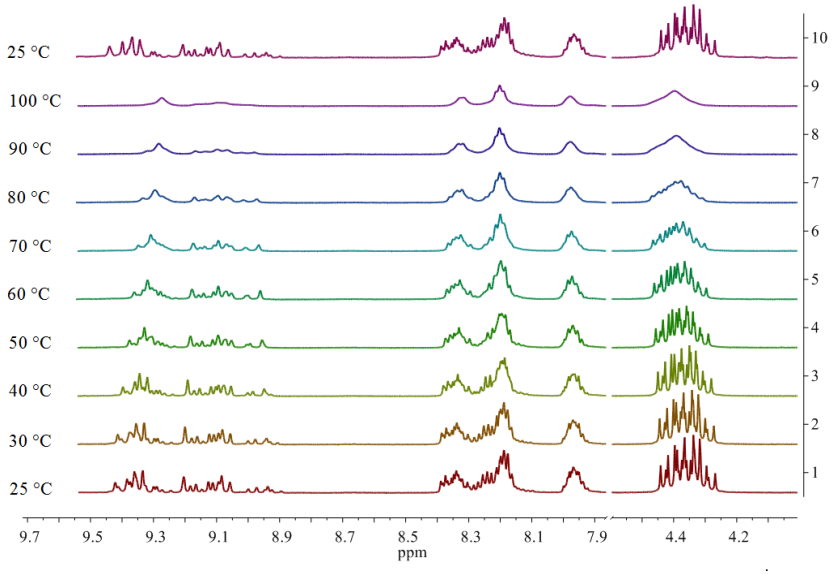
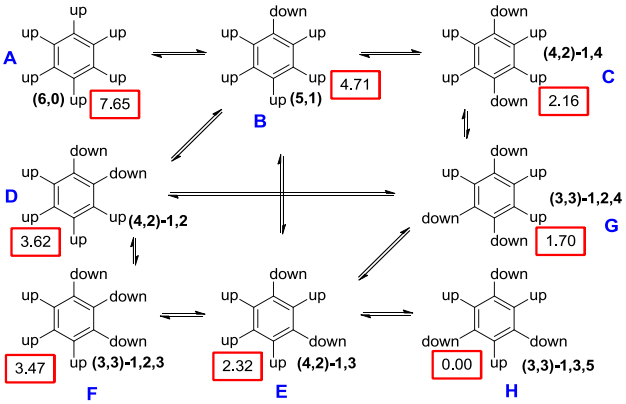


Figure 8: ^{1}H NMR spectra (600 MHz) of **88** in DMSO-d_6 with increasing temperature

Heating an NMR sample of **88** to 100 °C (Figure 8, spectra 1-9) followed by cooling down to rt (spectrum 10) also proved that **88** exists in different rotameric forms. In addition, spectrum 1 does not differ from spectrum 10, which led to the conclusion that salt **88** has a stable ratio between the formed rotamers at rt.

Similar to structure **87**, the synthesis of hexa(β-naphthyl)benzene, an arene analog of **87**, was reported by HARRINGTON et al.[65]. They also calculated minimized energies of eight different rotamers formed by hexa(β-naphthyl)benzene. The most stable rotamer is the one in which all β-naphthyl residues are twisted onto the same side (6,0). Likely, the minimized energies of these eight rotamers should not significantly differ in energies of

rotamers formed by **87** due to a very close chemical structure. In contrast, these energies must be different in the hexacationic salt **88** due to the repulsion of positively charged quinoline residues. Compound **88** as well as **87** form eight rotamers. Schematically, the rotamers can be classified as those in which *N*-methylquinoliniums residues are 6:0 (*all-syn*), 5-up/1-down, 4-up/2-down (1,2; 1,3; 1,4), and 3-up/3-down (1,2,3; 1,2,4; 1,3,5) (Scheme 56). The calculated energy differences between the rotamers are extremely small. The lowest energy rotamer is the 3-up-3-down (1,3,5) isomer whereas the *all-syn* (6,0) is 7.65 kJ·mol^{-1} and thus less stable.



Scheme 56: Eight energy-minimized rotamers of **88**, showing which can be directly interconverted by rotation of a single substituent and their relative energies (in kJ·mol^{-1}) are shown in red boxes

Hexaethylbenzene shows a similar behavior of rotamers[66]. Despite of small energy differences between the rotamers of **88**, an almost equal ratio between them cannot be assumed. Solving the simple combinatoric problem created by propeller-like compounds such as **87** or **88** results in the following ratio: **A**:**B**:**C**:**D**:**E**:**F**:**G**:**H**=1:6:3:6:6:3:6:1.

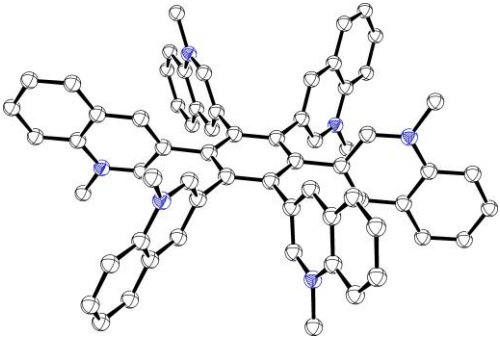


Figure 9: True minimum structure of the most stable rotamer of **88 (3,3)-1,3,5** (hydrogen atoms omitted for clarity)

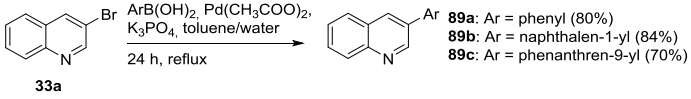
Calculations of all true minimum structures of **88** show that in all rotamers dihedral angles between quinoline and phenyl rings are in the range from 71 to 88°. The HOMO, as well as LUMO orbitals, are located on the six *N*-methylquinoliniumyl residues. The corresponding profiles are shown in supplementary materials in Figure 43 (page 268). The band gap is 3.93 eV.

3.3 3-Aryl substituted 1-methylquinolinium carbenes

As reported previously[64], trapping reactions of carbenes in quinolinium derivatives with alkynyl residues in 3-position were not successful. Therefore, an alternate pathway with the synthesis of biaryl compounds was developed in this chapter.

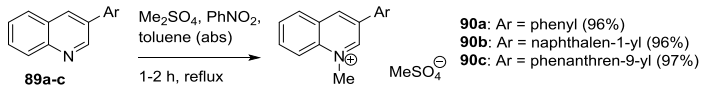
3.3.1 Synthesis of 1-methylquinolinium carbene precursors

First, starting compound 3-bromoquinoline **33a** was subjected to a Suzuki-Miyaura reaction with aryl boronic acids, 10% $Pd(CH_3COO)_2$ as a catalyst, and K_3PO_4 as a base in toluene/water solution to give 3-aryl quinolines **89a-c** (Scheme 57).



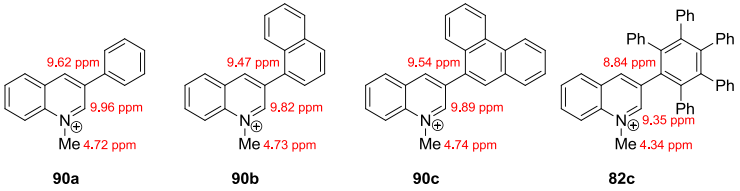
Scheme 57: Synthesis of 3-aryl quinolines **89a-c** by Suzuki-Miyaura coupling

The aryl residue at the third position of the quinoline ring likely plays the role of a bulky substituent for stabilization of the carbene carbon atom. Related to previous work[35], dimethyl sulfate was used as a convenient reagent for quaternization of quinolinium derivatives to obtain salts **90a-c** with high yields (Scheme 58). One drop of nitrobenzene was used as a catalyst in these reactions.



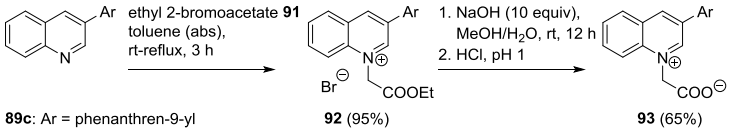
Scheme 58: Synthesis of 1-methyl-3-arylquinolinium methylsulfates **90a-c**

A proton in the second position of the quinoline ring displays the most downfield shift in ^{1}H NMR spectra of **90a-c**. A small but reproducible downfield shift of NCH_3 in the ^{1}H NMR spectra with increasing size of the substituent in the third position of quinoline was observed (Scheme 59).



Scheme 59: Characteristic ^{1}H NMR chemical shifts salts **90a-c**, **82c**

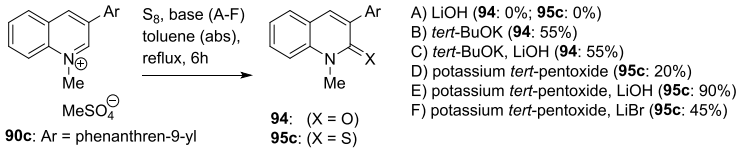
In addition, the reaction of quinoline **89c** and ethyl 2-bromoacetate **91** was performed (Scheme 60). Quinolinium derivative **92** was obtained with almost quantitative yield (95%) as a yellow powder, and was then successfully converted to a betaine **93** under basic conditions in 65% yield.



Scheme 60: Synthesis of betaine **93**

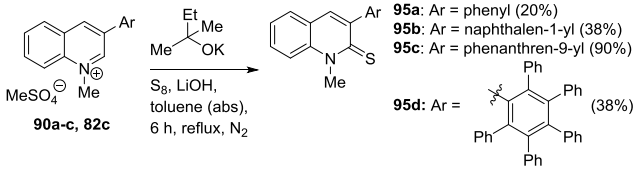
3.3.2 Trapping reactions

According to the research of LASSALETTA et al.[67] dealing with isoquinolinium salts, potassium *tert*-butoxide was tested as a base for the deprotonation of the salt **90c** in the presence of an excess of elemental sulfur in absolute toluene under reflux conditions. The product of the reaction resulted in an interaction between salt and base (Scheme 61, B). Interestingly, no sulfur-containing compound was found. 2D NMR spectra showed that the oxygen atom of **94** is connected to the C2 carbon of the quinoline ring. The C2 carbon atom gives the signal at 162.0 ppm in the ^{13}C NMR spectrum. Additionally, the compound was proven *via* HRMS. Addition of LiOH to the reaction mixture did not change the result of the reaction. However, using potassium *tert*-pentoxide led to a color change during the reaction and gave thione **95c** as an orange solid compound with a yield of 20%. The same reaction including 1.2 equiv of potassium *tert*-pentoxide and 10 equiv of LiOH increased the yield to 90%. Changing from LiOH to LiBr also led to an increased yield of product (45%) compared to conditions without lithium compounds. However, the addition of potassium *tert*-pentoxide proved vital as LiOH alone did not give successful results either (Scheme 61).



Scheme 61: Trapping reaction of salt **90c** with sulfur under different conditions

Based on the obtained information, mineral lithium compounds are likely to stabilize the carbene formed *in situ* by forming a covalent bond between lithium and the C2 carbon atom. Therefore, using a mixture of LiOH and potassium *tert*-pentoxide (1.2 equiv), thiones **95a-d** were obtained and separated by column chromatography successfully (Scheme 62).



Scheme 62: Trapping reactions of salts **90a-c**, **82c** with sulfur by optimized conditions

All thiones are orange solid compounds with a specific odor. Chemical signals of the C=S carbon atoms in $CDCl_3$ are shifted more downfield compared to the C=O signal and adopt values of 185.0, 185.4, 185.3, and 184.7 ppm, respectively. The structure of **95b** was proven by X-ray structure analysis (Figure 10). Single crystals of thione **95b** were obtained by slow evaporation of a concentrated solution in chloroform. The compound crystallized orthorhombic. The C=S double bond has a length of 168.39(18) pm. The typical Csp^2=S double bond length is in the range from 159.9 to 161.1 pm, whereas the Csp^2-S single bond length is 177 pm[68]. The dihedral angle between the quinoline and naphthalene planes is 76.245°.

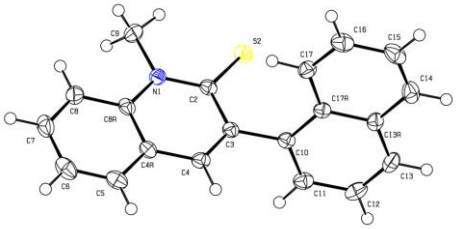
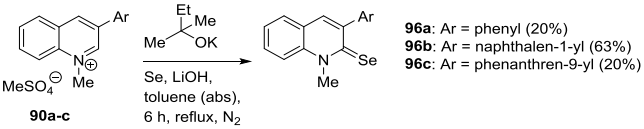


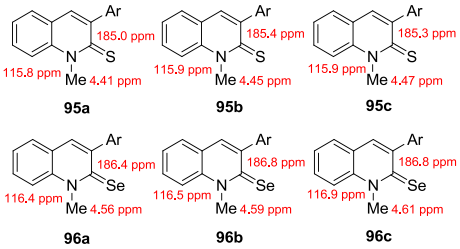
Figure 10: Crystal structure determination of thione **95b**

Reactions of 3-aryl quinolinium salts with elemental selenium were also investigated. In this case, reactions of quinolinium salts **90a-c** with selenium were successful, however, in lower yields in comparison to the thione formations (Scheme 63).



Scheme 63: Trapping reactions of salts **90a-c** with selenium

The determination of the structures of the obtained selenones proved to be challenging. According to 2D NMR spectra, selenium was connected to the C2 carbon atom of the quinoline ring, but ^{13}C chemical shifts of C2 atoms were very close to the C2 carbon atom in thiones and have values of 186.4, 186.8, 186.8 ppm, respectively, while the difference between C=O and C=S in **94** and **95c** is 23.3 ppm in chloroform (Scheme 64). Nevertheless, chemical shifts of methyl groups in deuterated chloroform are significantly different.



Scheme 64: Characteristic NMR signals of thiones **95a-c** and selenones **96a-c** in $CDCl_3$

In addition, the structure of **96c** was proven by X-ray structure analysis (Figure 11). Single crystals of selenone **96c** were obtained by diffusion of cyclohexane in its solution in chloroform. The compound crystallized monoclinic. The C=Se double bond has a length of 183.8(2) pm. The typical Csp^2=Se double bond length is 171 pm[69] and the typical Csp^2-Se single bond length is 189 pm[68]. The dihedral angle between the quinoline and naphthalene planes is 70.077°. The bond lengths of C-X (X: S, Se) can be explained by mesomeric structures including zwitterionic forms. In addition, ^{13}C chemical of C8 carbon atoms of quinolines of neutral **89a-c** are in the range from 129.3 to 129.5 ppm in $CDCl_3$, whereas in corresponding thiones **95a-c** signals are at 115.8,

115.9, and 115.9 ppm, and for selenones **96a-c** signals are at 116.4, 116.5, 116.9 ppm, respectively, which is comparable to the C8 carbon atom signals (119 ppm) of the salts **90a-c** in DMSO-d_6.

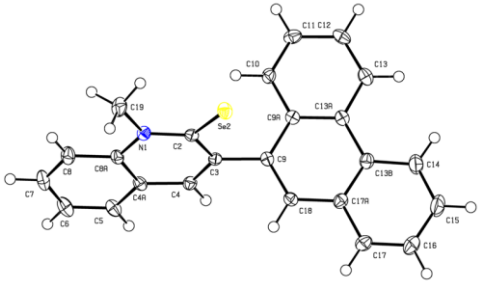
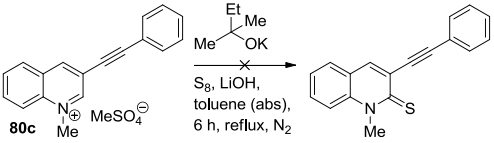


Figure 11: Crystal structure determination of **96c**

All selenones are red-colored compounds with a specific odor. Furthermore, the bulkier the aromatic substituent, the higher the melting point in thiones and selenones. E. g., the selenone with a phenanthrenyl residue (**96c**) has a melting point of 271 °C, while the selenone with a phenyl residue (**96a**) is an oil. Analog reactions with tellurium were not successful.

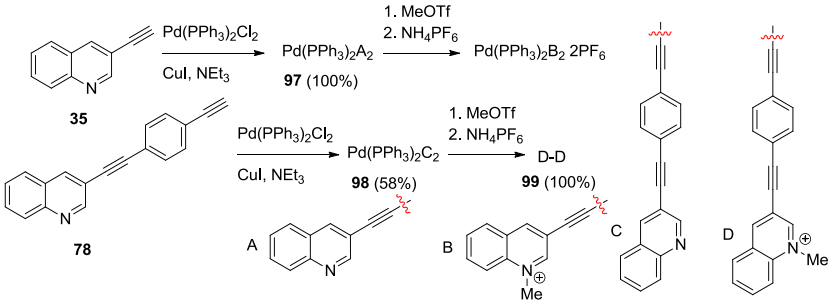
The same conditions have been performed in reactions with quinolinium salts which contain an alkynyl residue in the third position (**42a**, **43**, **80c**) instead of an aromatic ring, but they did not give successful results (Scheme 65).



Scheme 65: Trapping reaction of salt **80c** with sulfur

The reaction of π-extended 3-ethynylquinoline derivative **78** was tested with $Pd(PPh_3)_2Cl_2$, in analogy to **35** described by SMEYANOV[64], followed by methylation with

MeOTf (Scheme 66). However, only the dicationic salt **99** was obtained in quantitative yield.

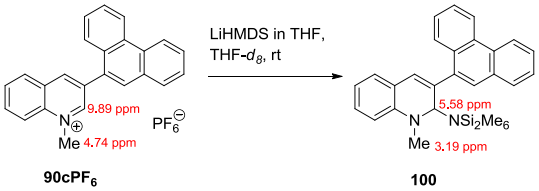


Scheme 66: Reactions of ethynyl quinolines (**35**, **78**) with Pd complex followed by methylation

3.3.3 NMR investigations of 3-aryl quinolinium salt with bases

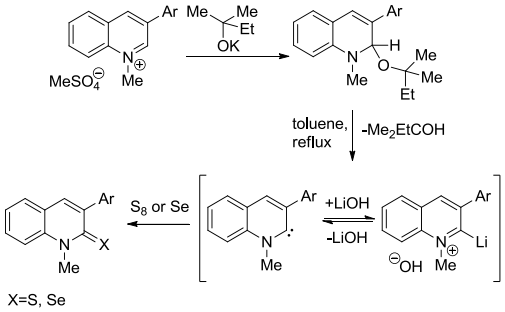
Deprotonations of the quinolinium salts by a base-screening in combination with NMR experiments were performed next. The deprotonation of salt **90c** with bases such as potassium *tert*-pentoxide and lithium *bis*(trimethylsilyl)amide was examined in DMSO-d_6, benzene-d_6, and THF-d_8. To increase the solubility of the salt in acetonitrile-d_3, the methylsulfate anion was exchanged to hexafluorophosphate by precipitation of the corresponding salt in aqueous solution.

Exact reaction conditions could not be examined in an NMR tube, due to insolubility of salt **90c** in toluene or benzene. Addition of potassium *tert*-pentoxide to a solution of salt **90c** in DMSO-d_6 at rt lead to an upfield shift of protons, which most likely indicates the absence of a positive charge in the reaction product. However, the results cannot be described due to impurities which are visible in the received spectrum. A similar pattern is observed when replacing DMSO to other solvents, e. g. THF or acetonitrile, and using another base, such as LiHMDS instead of potassium *tert*-pentoxide. Fortunately, using LiHMDS in THF-d_8 showed that the product of the reaction is compound **100** (Scheme 67).



Scheme 67: Reaction of salt **90cPF$_6$** with LiHMDS in THF and characteristic chemical shifts

According to the obtained results, the carbene formation proceeds most likely through the thermolysis of **90c** and not through deprotonation as in case of imidazolium or other five-membered electron-rich heterocycles[38] (Scheme 68).

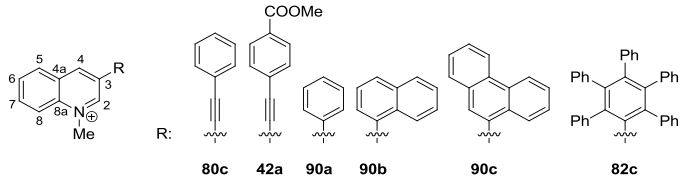


Scheme 68: Proposed mechanism of trapping with sulfur and selenium

The presence of lithium ions stabilizes the carbene, and cause higher yields of the reactions with sulfur and selenium.

In contrast to the aromatic substituents in the salts **90a-c**, **82c**, the acetylenic residues in salts **42a**, **80c**, **43** are conjugated with the quinoline ring and include an additional mesomeric effect. This resulted in a different value of electronegativity of C3 carbon atoms of quinoline. "The greater the electronegativity of the atom or group, the lower the electron density around the proton, and the further downfield the chemical shift"[60]. Electronegativity can be obtained using NMR spectra, when magnetically anisotropic groups as benzene rings or C≡C triple bonds[60] are absent. As evidence of different

electronegativity on the C3 carbon atom, ^{13}C NMR carbon shifts of some methylquinolinium salts are given in Table 1.



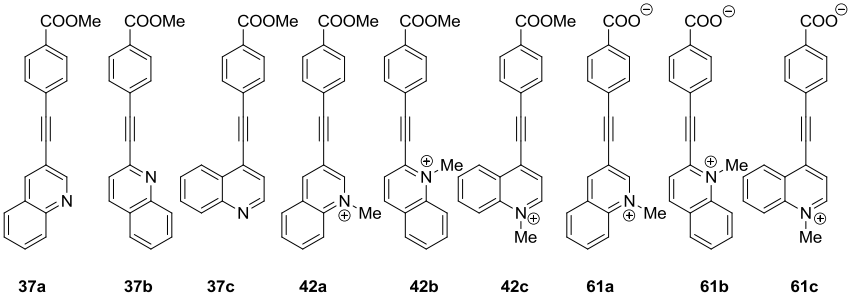
	80c	**42a**	**90a**	**90b**	**90c**	**82c**
C2	153.1	152.2	149.3	151.1	151.1	150.6
C3	**116.7**	**116.2**	**133.5**	**133.4**	**133.5**	**134.4**
C4	147.9	148.3	142.9	146.6	146.7	147.5
C4a	128.7	130.5	129.2	129.2	129.2	127.7
C5	130.2	130.4	130.5	130.5	130.5	129.9
C6	130.3	130.7	130.2	130.2	130.2	130.5
C7	136.0	136.3	135.2	135.4	135.5	135.5
C8	119.2	119.3	119.0	119.0	119.0	118.9
C8a	137.3	137.5	137.2	137.5	137.7	135.5
NCH_3	45.4	45.5	45.4	45.3	45.3	44.8

Table 1: ^{13}C NMR chemical shifts of some methylquinolinium salts

Table 1 shows that C3 carbon atom connected to the C≡C triple bond has a higher electron density compared to the electron density of aryl substituted quinolinium derivatives. Likely, it is the main reason why the salts **42a**, **80c**, **43** do not react with sulfur, and therefore, the nucleophilic addition with potassium *tert*-pentoxide cannot be realized according to the mechanism proposed previously.

3.4 Physical properties and calculations of obtained betaines and related compounds

Calculations, as well as spectroscopic examinations, were performed to elucidate the bonding properties of the neutral compounds **37a-c**, salts **42a-c**, and betaines **61a-c** (Scheme 69).



Scheme 69: Chemical structures of discussed compounds

3.4.1 DFT calculations of quinolinium salt precursors

HOMO-LUMO profiles are comparable for **37a-c**: each frontier orbital is completely delocalized on the entire molecular systems (Figure 12). The band gap is 3.88, 3.92, and 3.79 eV for **37a**, **37b**, and **37c**, respectively.

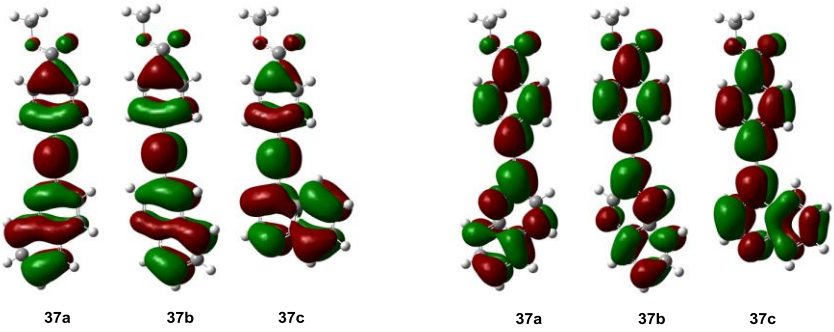


Figure 12: HOMO (left) and LUMO (right) profiles of quinolines **37a**, **37b** and **37c**, respectively

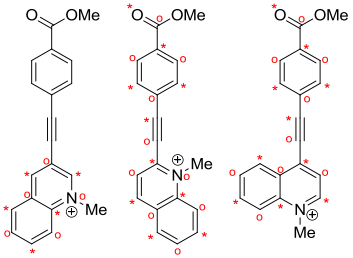
The triple bonds of the esters **37a-c** gave no signals of absorption in the region of stretching vibrations for the triple bond (ν: 2200-2400 cm^{-1}). According to their Raman spectra, the wavenumbers of the C≡C triple bonds of **37a-c** are almost equal with the values of 2015, 2018, and 2018 cm^{-1} for **37a**, **37b**, and **37c**, respectively.

3.4.2 DFT calculations, IR, and Raman spectra of π-extended quinolinium salts

The chemical behavior of mesomeric betaines can be analyzed by application of

- ♦ Dewar's/Coulson's concept
- ♦ frontier orbital profiles, and
- ♦ the idea of mesomerism.

Dewar´s/Coulson´s concept was first introduced to identify alternant and non-alternant hydrocarbons by assigning stars to all odd numbered positions of the organic framework. In alternant hydrocarbons, no atoms of the same set are directly linked, whereas in non-alternant two starred or two non-starred positions are adjacent[70]. In contrast to the neutral compounds **37a-c**, the behavior of their salts is different. In the case of the 3-substituted isomer **42a**, the triple bond is connected *via* an unstarred position to the quinoline ring on the application of Dewar's/Coulson's concept, where unstarred positions are marked by an "o". These positions are nodal (inactive) positions in the frontier orbital profile. The carbons of the C≡C triple bonds in 2- and 4-substituted isomers **42b** and **42c** are linked *via* a starred (active; no nodal position in the HOMO) position (Scheme 70).



Scheme 70: The active and inactive atoms in salts **42a-c**

By inspection of the mesomeric structures of the corresponding salts, one can conclude that active atoms are located where the positive charge is delocalized in the mesomeric structures, i.e., at atoms with electron sextet structures.

The HOMOs of compounds **42a-c** are similar to each other and are localized throughout the π-conjugated system of the molecules, while the LUMO profiles, as well as band gaps of the quinolinium salts **42a-c**, differ between **42a** and **42b**, **c** (Figure 13). The band gaps are 2.73, 3.25, and 3.06 eV for the compounds **42a**, **42b**, and **42c**, respectively. The positive charge distributions according to the canonical formulae are reflected by the LUMO atomic orbital coefficients. The largest Fukui indices are located on carbon atoms with electron sextet structures in the mesomeric forms of the salts. In salt **42a** the positive charge is only delocalized in the quinolinium ring, whereas in salts **42b**, **c** in the entire molecules.

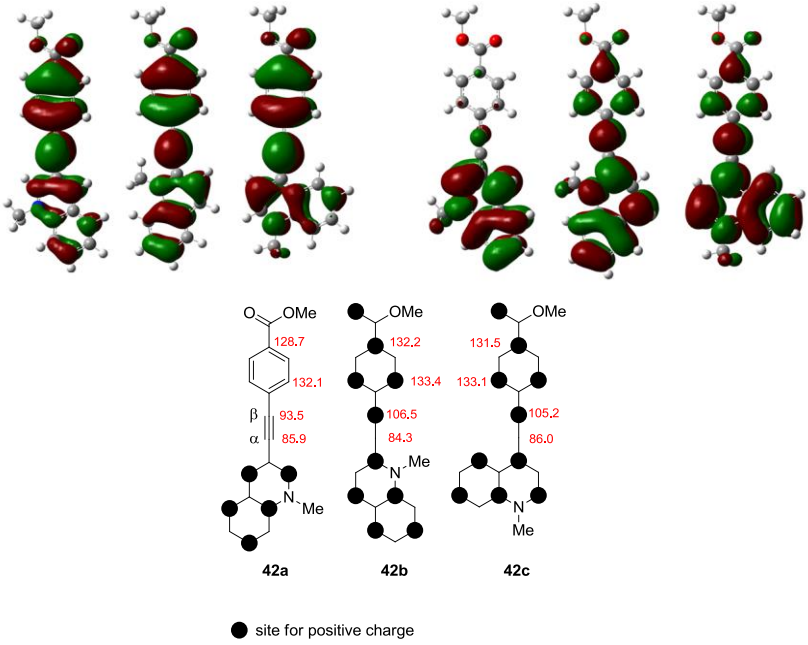
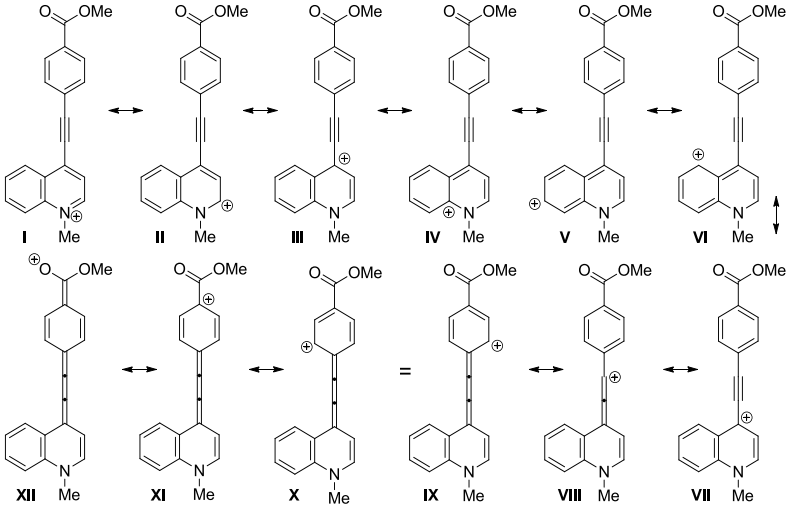


Figure 13: HOMO (left) and LUMO (right) profiles of salts **42a**, **42b,** and **42c**, respectively; Charge distribution according to the mesomeric structures of salts **42a-c**. Some characteristic ^{13}C NMR signals marked in red

The observed characteristic ^{13}C NMR chemical shifts serve as a confirmation of the difference between **42a** and **42b**, **c**. As an example, the Cβ carbon atom of the C≡C triple bond of salt **42a** gives the value of 93.5 ppm in ^{13}C NMR, whereas analogous ones in **42b**, **c** give the signals at 106.6 and 105.2 ppm, respectively. This comparison of the chemical shifts indicates the delocalization of the positive charge on the Cβ carbon atom in **42b**, **c**, and the absence of the delocalization in **42a**. The mesomeric structures of salt **42c** are given in Scheme 71.



Scheme 71: Mesomeric structures of **42c** (**I**-**XII**) which describe the delocalization of the positive charge in the molecule

The IR spectra also support the suggestion of different positive charge delocalization in the isomers **42a-c**. The absorption of the stretching vibration of the triple bond was observed (Figure 14). However, the absorption peak for the 3-substituted isomer **42a** shows a very weak intensity at 2227 cm^{-1}, whereas the 2- and 4-substituted molecules **42b**, **c** gave the absorption band with medium intensity at 2206 and 2209 cm^{-1}, respectively.

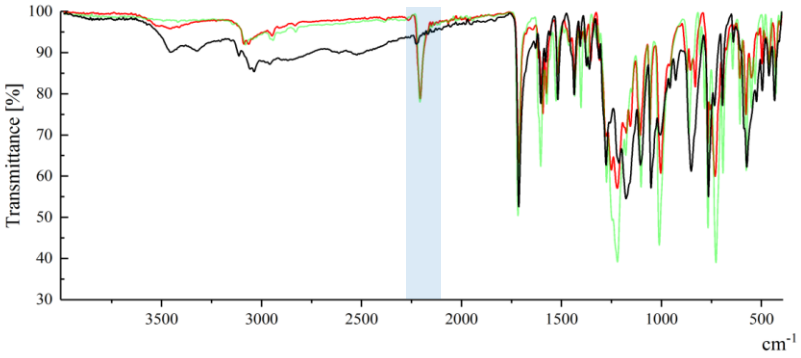


Figure 14: IR spectra of **42a-c** (**42a**-black line, **42b**-red line, **42c**-green line)

The Raman spectra showed similar absorption values of the triple bonds of 2229, 2206, and 2212 cm^{-1}, respectively. The calculations of the Raman spectra were performed using a 6-311g(d,p) basis set, within the frame of the DFT theory at the b3lyp level (Figure **40**, supplementary). The stretching vibration of the triple bond gave the most intense signal in the spectra of **42a-c**. The calculated values of the ν(C≡C) vibration are 2295 (**42a**), 2269 (**42b**) and 2265 cm^{-1} (**42c**). The difference of the stretching vibration of the triple bond between **42a** (3-yl) and **42b** (2-yl) is 26 cm^{-1}, and close to the experimental value of 23 cm^{-1}. However, a greater deviation occurs between **42a** (3-yl) and **42c** (4-yl) comparing the calculated (30 cm^{-1}) and the experimental (17 cm^{-1}) one. The reason can be the intermolecular interactions existing in solid samples, which are absent in the theoretical model. For a more quantitative description of the contribution of the positive charge in the canonical formulae (**42cVIII-XII**, Scheme 71) of the salts **42b**, **c**, two model molecules (H_3C-C≡C-CH_3 and H_2C=C=C=CH_2) were used with the same theoretical approach to calculate wavenumbers of the pure triple bond and in the cumulene system. The predicted values were 2365 and 2205 cm^{-1}, respectively. The difference (160 cm^{-1}) showed a contrast between two pure forms. According to this fact, contributions of the positive charge in the cumulenoid formulae are quantified as 14-15% for **42b** and 10-11% for **42c**.

3.4.3 DFT calculations of π-extended quinolinium betaines 61a-c

The calculated HOMO/LUMO profiles of carboxylate **61a** confirm the CCMB-type cross-conjugation[33,71] (Figure 15), in which the triple bond is connected *via* a nodal (unstarred) position which causes an interruption of the π-conjugation. The HOMO orbitals are essentially located on the carboxylic group, and the LUMOs are on the quinoline ring and are in agreement with the canonical forms. In the betaines, the active atoms are on positions of delocalized positive and negative charges. The marked difference between the salts **42a** and **42b**, **c** is observed in betaines **61a-c** as well. The band gap is 0.42, 1.07, and 1.07 eV for compounds **61a**, **61b**, and **61c**, respectively. In the case of betaine **61a**, delocalization of the positive charge does not influence the stability of the molecule and form a CCMB, whereas betaines **61b, c** proved to be unstable. Canonical formulas and frontier orbitals help to understand their instabilities. The LUMO profiles of compounds **61b, c** are similar to the LUMOs of their salts and located in the entire π-electron system.

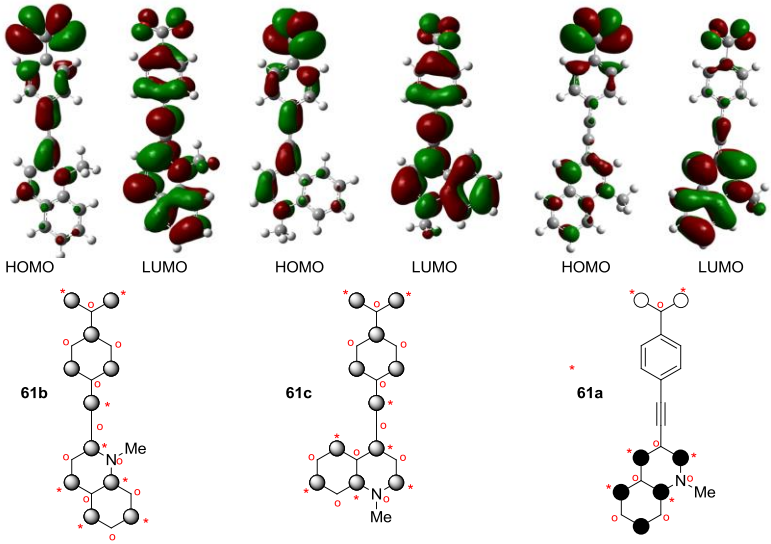
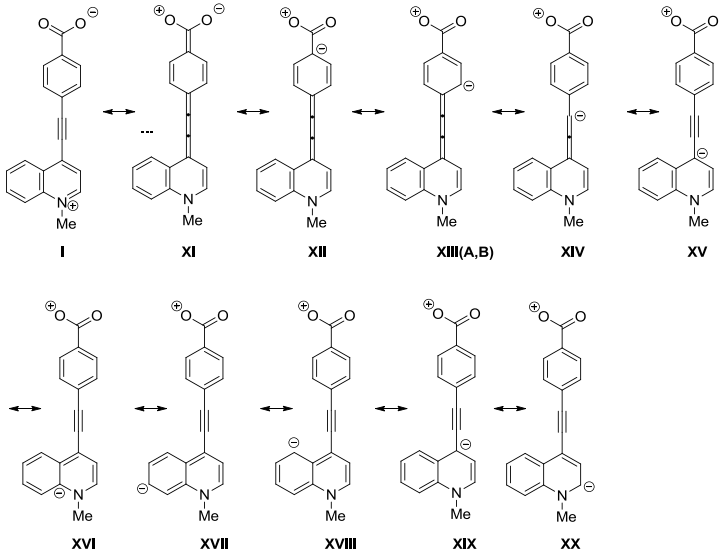


Figure 15: Charge distribution according to the mesomeric structures of **61a-c** and their HOMO/LUMO profiles

The HOMOs are also in agreement with canonical formulae and possess their largest coefficients in the carboxylate group with contributions in the phenyl ring, the triple bond and the quinolinium ring (Figure 15, Scheme 72). Canonical forms (**61cXI-XX**) show delocalization of the negative charge not only in the carboxylic group but also in the residual molecule. In the same time, the positive charge is delocalized only in the carboxylic group. The contribution of each canonical form with an electron sextet structure on oxygen atoms (mesomeric structures **61cXI-XX**) compared to carbon atoms is smaller due to the rules of resonance[60].



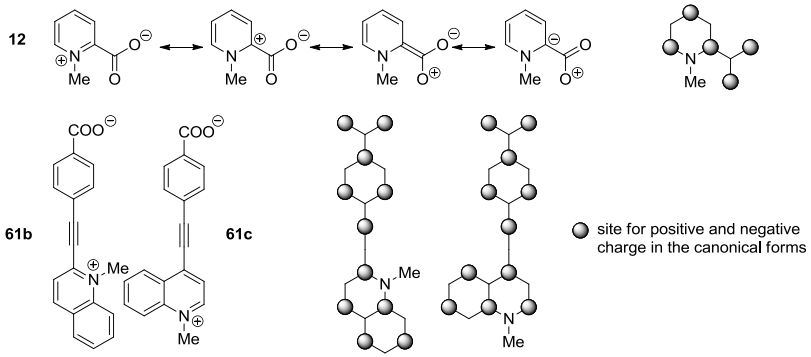
Scheme 72: Dipolar mesomeric structures of **61cI-XX**

However, the extending of the conjugated system increases the number of canonical forms with electron sextet structures on oxygen atoms (bigger contribution in total). Thus, the stability of the molecule decreases. Addition of the base to compound **42c** lead to decomposition of formed betaine **61c** within 0.5 h in an NMR tube.

3.4.4 Structural features of betaines

In order to prove the relevance of the charge delocalization according to the canonical formulae of **61a-c** by HOMO/LUMO profiles of the betaines, DFT calculations were performed.

In the previous chapter betaines **61b, c** were considered, and their instability was explained. An additional example of a PCCMB is the alkaloid *Homarine* **12**[33]. Betaines **61b**, **c** are the π-extended analogs of **12**. The compound **12** is not stable at temperatures higher than 30 °C and does not have a melting point[72] (Scheme 73).



Scheme 73: Charge distributions according to the mesomeric structures of *Homarine* **12**, and betaines **61b**, **c**

According to the canonical formulae of *Homarine* **12**, the positive and negative charges are delocalized in the entire π-conjugated system. However, its HOMO/LUMO profile[33] is similar to the frontier orbitals of *Trigonelline* **11** which belongs to CCMBs (Figure 16). In both molecules, the positive charge is delocalized in the pyridinium ring, whereas the negative charge is located on the carboxylic group. According to these DFT calculations *Homarine* **12** should be classified as CCMB.

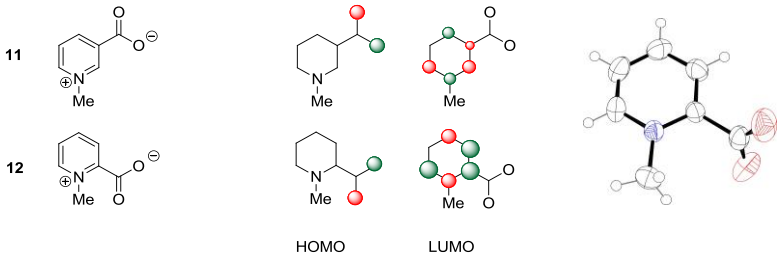
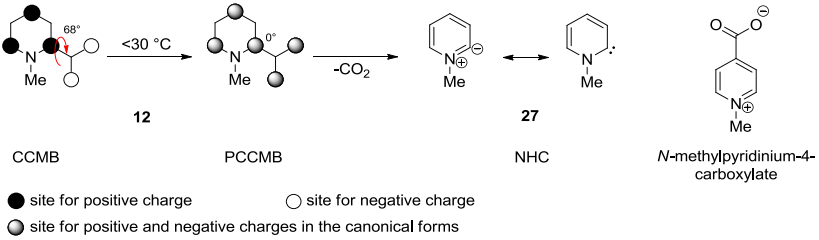


Figure 16: *Trigonelline* **11** and *Homarine* **12** and their HOMO/LUMO profiles (left). Crystal structure of *Homarine* (right)

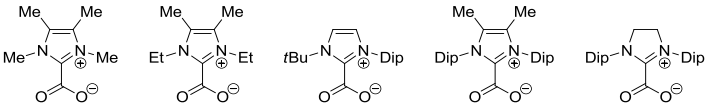
The X-ray analysis of the crystal structure of *Homarine* **12** shows that the dihedral angle between the carboxylic group and the pyridinium ring is 68° due to the intramolecular hydrogen bonds formation[72]. In fact, the carboxylic group is not conjugated with pyridinium ring. Likely, the absence of the conjugation stabilizes the molecule, and that is why *Homarine* **12** could be found in nature and exists as CCMB (Scheme 74). *N*-Methylpyridinium-4-carboxylate, another isomer of **12**, can be classified as PCCMB. This compound exists as a monohydrate[73] with a melting point of 291 °C[73] and has not been found in the anhydrous form so far.



Scheme 74 Proposed CCMB – PCCMB interconversion of *Homarine* **12**

Other examples of an influence of the dihedral angles on the conjugation are PCCMBs **101a-e**. The X-ray analysis of betaines **101a-e**, described by JANIS LOUIE[74], shows that in all cases the carboxylic group does not lie in one plane to the heterocycle (Scheme 75). In the betaines **101b-e**, the carboxylic group is not conjugated with the heterocyclic ring, because the dihedral angle is greater than 30°. Theoretically, these

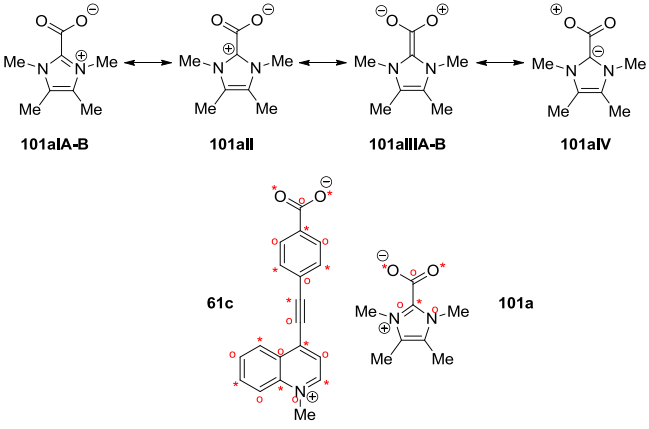
betaines can be classified as CCMBs. Merely betaine **101a** exists as a PCCMB in the solid state as it is only slightly twisted (dihedral angle < 30°).



101a **101b** **101c** **101d** **101e**

Scheme 75: Five-membered electron-rich PCCMBs **101a-d** and saturated analog **101e**

In comparison to the unstable betaine **61c**, the stability of betaine **101a** can be explained by a lesser number of the active (starred) positions (Scheme 76). Therefore, the positive charge cannot be "localized" in the carboxylic group as effectively as in the case of **61c**. In addition, imidazolium derivative **101a** is a five-membered electron-rich heterocycle in contrast to the electron-poor quinolinium derivative **61c**. Thus, it is possible to conclude that the contribution of mesomeric structure **101aIV** is low.



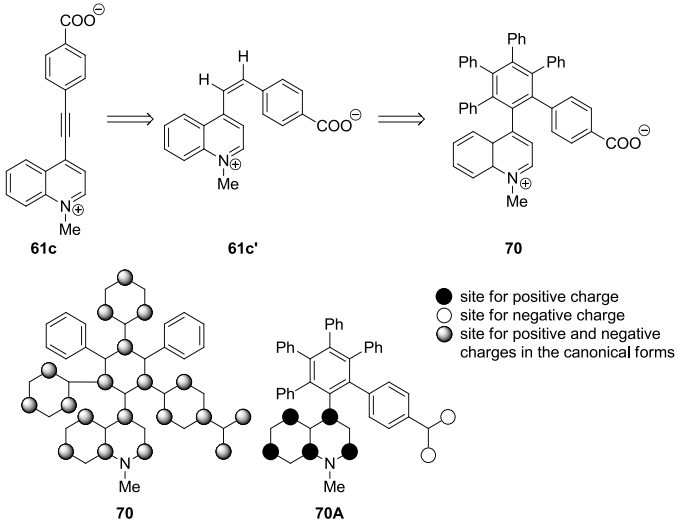
101aIA-B **101aII** **101aIIIA-B** **101aIV**

61c **101a**

Scheme 76: Canonical forms of **101a** and the active (starred) atoms of **61c** and **101a**

Replacement of the C≡C triple bond to a C=C double bond does not change the classification of hypothetical betaine **61c′** (Scheme 77). MB **61c′** also belongs to

PCCMB and most likely should be unstable. In the case of a triple bond conjugation, a change of angle *via* rotation does not have an impact on conjugation due to the π-electron cloud around the C≡C triple bond. However, compounds with C=C double bonds cannot be conjugated, if the π-orbital of the neighboring atom does not overlap with conjugated moieties (angle more than 30°). To illustrate the influence of dihedral angles on conjugation in betaines, compound **70** was synthesized. Betaine **70** has a propeller-like structure, similar to other six-aryl-substituted benzenes. Each of its six residues is not conjugated with the central benzene ring. As a result, the positive charge is delocalized only on the quinolinium moiety, whereas the negative charge is located only on the carboxylic group. The representation of the charge distribution according to the mesomeric structures of betaine **70** is not sufficient and it cannot be classified as PCCMB and should consequently be considered as CCMB (Scheme 77, compound **70A**).



Scheme 77: Structural features of MBs

The calculations of the true minimum structure of **70** as well as DFT calculations were performed. The calculated structure of MB **70** is given in Figure 17. The bending of the

positively charged quinoline moiety and the negatively charged carboxylic group in a direction of each other likely is a result of an attractive interaction between them. Characteristic distances showing this attraction are also given in the following figure. Additionally, the distance between the oxygen and the C2 carbon is 295 pm, and the angle C2-H2···O is 125° corresponding to the internal hydrogen bond. The calculated dihedral angle between the quinolinium ring and the central benzene ring is 73°, and between the *p*-carboxy-substituted phenyl ring and the central phenyl ring is 82°, respectively.

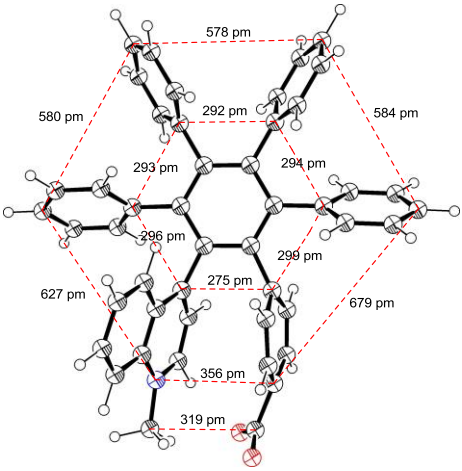


Figure 17: True minimum structure of MB **70**

The calculated HOMO/LUMO profiles confirm the proposed charge distribution **70A** (Figure 18). The HOMO orbitals are located on the carboxylic group, and the LUMOs are on the quinoline ring. The band gap is 1.78 eV.

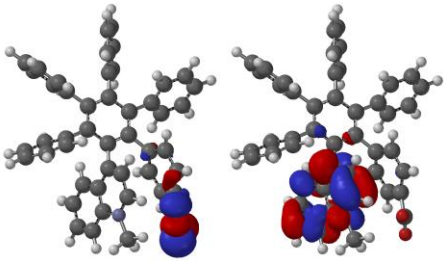
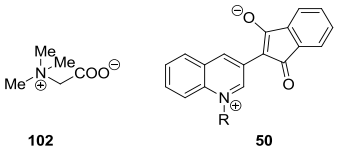


Figure 18: HOMO/LUMO profiles of MB **70**

3.4.5 Charge distribution in betaines

Different factors take influence on the solubility of compounds such as temperature, pressure, the presence of other chemicals as well as physical and chemical properties of the dissolved compound and solvent. The widely known aphorism "*like dissolves like*", also expressed in the Latin language as "*Similia similibus solvuntur*", is the simplistic but useful rule of thumb to indicate that a solute will dissolve better in a solvent, which has a similar chemical structure. REICHARDT[75] defines "solvent polarity" as the overall solvation capability of solvents. Polar compounds are soluble in polar solvents such as water, less soluble in the fairly polar methanol and not soluble in non-polar solvents such as benzene and *vice versa*.

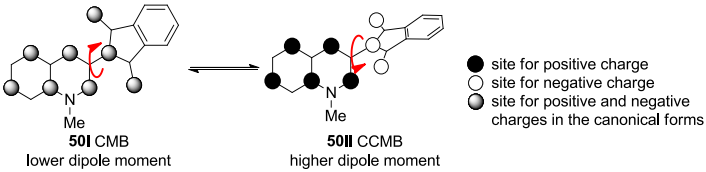
JINDONG WANG[76] showed that solubility of original *Betaine*, trimethylglycine **102** (Scheme 78), is higher in strongly polar solvents compared to weak and moderately polar solvents. The solubility was tested in water, methanol, ethanol, *n*-propanol, 2-propanol, *n*-butanol, and other solvents[77]. He also showed that the solubility of trimethylglycine **102** in acetic acid and ethylene glycol is higher than in DMSO. Likely, it can be explained by protonation of betaine and formation of the salt of trimethylglycine **102** in acetic acid.



102 **50**

Scheme 78: Trimethylglycine **102** (*Betaine*) and MB **50**

However, betaine **50** has two non-isolated charges and the understanding of the solubility mechanism of HMBs is more difficult due to delocalization of both negative and the positive charges in conjugated systems. Obviously, the contribution of each mesomeric structure is different. Abovementioned, the classification of MBs to my opinion depends in some cases on dihedral angles in molecules. Based on this fact, changing the dihedral angle (planar system – twisted system) can lead to a change of betaine classes as well as its dipole moment (Scheme 79).



50I CMB
lower dipole moment

50II CCMB
higher dipole moment

Scheme 79: Proposed CMB-CCMB dihedral angle interconversions of **50**

Likely, in polar solvents compound **50** exists as form **50II** (higher dipole moment of compound **50**), and in nonpolar as **50I** (lower dipole moment). X-ray analysis of hydrochloric derivative **50×HCl** indicates that the dihedral angle between the quinoline ring and the indanedione ring is 9.001° (Figure 19). Furthermore, the molecule has an internal hydrogen bond C2—H2···O10 with a bond length of 224.75(1) pm and an angle of 129.299(2)°. In addition, the C3—C9 bond length is 145.84(0) pm which corresponds to the length of the C-C single bond. However, the crystal structure of derivative **50×HCl** cannot provide structural information about betaine **50** and behavior in solutions.

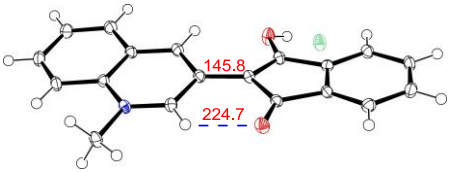
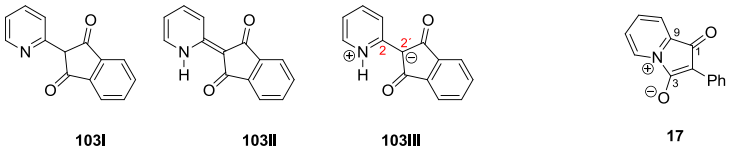


Figure 19: Crystal structure of **50×HCl**

KEMME[78] determined the fine structure of α-pyrophthalone **103** (quinoline yellow **104** is its benzo-derivative) by X-ray diffraction analysis and ^{1}H NMR spectroscopy from three proposed structures (Scheme 80).



Scheme 80: Pyrophthalone **103**, MB **17** synthesized by POTTS

According to the X-ray analysis, the dihedral angle between the pyridine ring and the indanedione ring is 5° stabilized by internal hydrogen bond N1—H···O11 with an angle of 140° and an N···O distance of 273 pm. The C2—C2′ bond length is 141.2 pm, whereas the typical C=C double bond length is 134 pm. The X-ray crystal data excludes tautomer **103I**. As an evidence of dipolar structure **103III** (also called "*intraionic structure"* by those authors) in the solid state KEMME used the fact that molecules of **103** are packed within the crystal as molecular self-complexes. In the molecular self-complexes, the donor fragment of one molecule is located above the acceptor fragment of another molecule[79]. This hypothesis is supported by facts that compound **103** has a high dipole moment and melting point, and a low solubility[78]. X-ray data of **103** were also obtained by DOBOSZ[80] (Figure 20). He also proved the *zwitterionic* form of **103III**. The C2—C2′ bond length is 141.9(3) pm. Also, other neutral compounds similar to **103** with *zwitterionic* forms and single bond character in crystals are known[81]. In comparison to α-pyrophthalone **103**, the natural compound *Tyrian purple* **105** does not

form self-complexes. The C-C bond length between the two indole rings is 136.5 pm[82] which corresponds to the length of the C=C double bond.

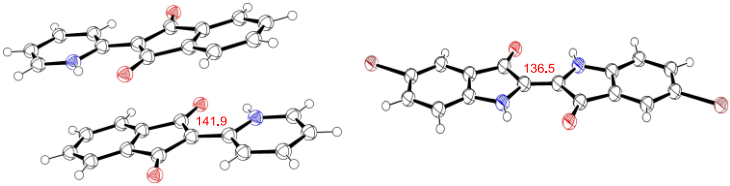


Figure 20: An example of molecular self-complex in the crystal structure of **103** by DOBOSZ (left), and the crystal structure of *Tyrian purple* **105** (right)

The calculations of the minimum structure of **50** by different conditions were performed (Figure 21). The C3-C9 bond length is 141.79, 142.64 and 143.68 pm *in vacuo*, benzene, and DMSO, respectively. The calculated C3-C9 bond length of betaine **50** is comparable to analogous bond length in **103**. In all three cases (*vacuum*, benzene, DMSO), the structure of **50** is planar with a dihedral angle of less than 1°. The calculation of the dipole moment of betaine **50** shows that it increases from 8.51 D in *vacuo* (single molecule) to 10.40 D (benzene) and to 12.63 D (DMSO).

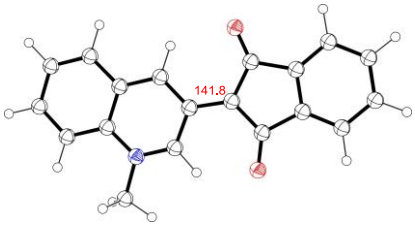
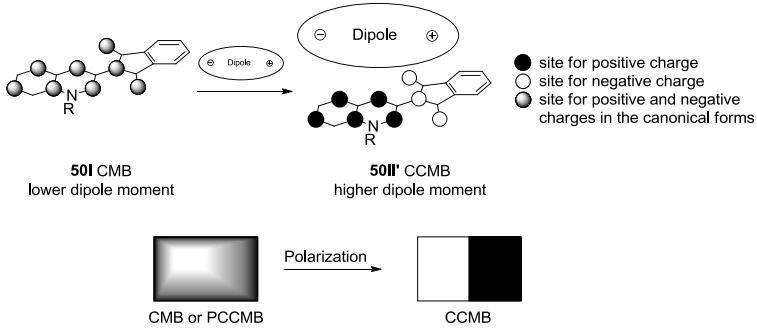


Figure 21: Calculated true minimum structure of **50** *in vacuo*

Based on crystal data analysis and calculations one can conclude the following deduction: first, all mesomeric betaines may display a cross-conjugated behavior in dependence on external parameters even if they are not twisted. Thus, neighboring molecules (molecules of itself as well as molecules of solvents) can polarize betaines even if they are planar (Scheme 81); second, the bond lengths cannot be used as a mere criterion for a classification of betaines. Thus, likely this also explains the C-N single

bond character in X-ray data of the planar MB **17** (Scheme 80) obtained by POTTS[26,27] On extension of the view on heterocyclic mesomeric betaines in such a way, to my opinion, the physical existence of what has been named "union bond" in PCCMBs is questionable.



Scheme 81: Polarization of MBs

To support the proposed theory about the polarization of betaines, ^{1}H NMR spectra of HMB **50** were measured in 13 deuterated solvents such as benzene (0.00 D), toluene (0.36 D), pyridine (2.20 D), 2-propanol (1.66 D), ethanol (1.69 D), methanol (1.70 D), chloroform (1.04 D), dichloromethane (1.60 D), 1,4-dioxane (0.45 D), THF (1.75 D), DMF (3.82 D), acetonitrile (3.92 D), and DMSO (3.96 D). Interestingly, MB **50** is insoluble in water (1.85 D) and cyclohexane (0.00 D), no signals in the ^{1}H NMR spectra were observed. In addition, in ethanol betaine **50** is almost insoluble (according to ^{1}H NMR). The ^{1}H NMR spectrum of betaine **50** in DMSO-d_6 is given in Figure 22.

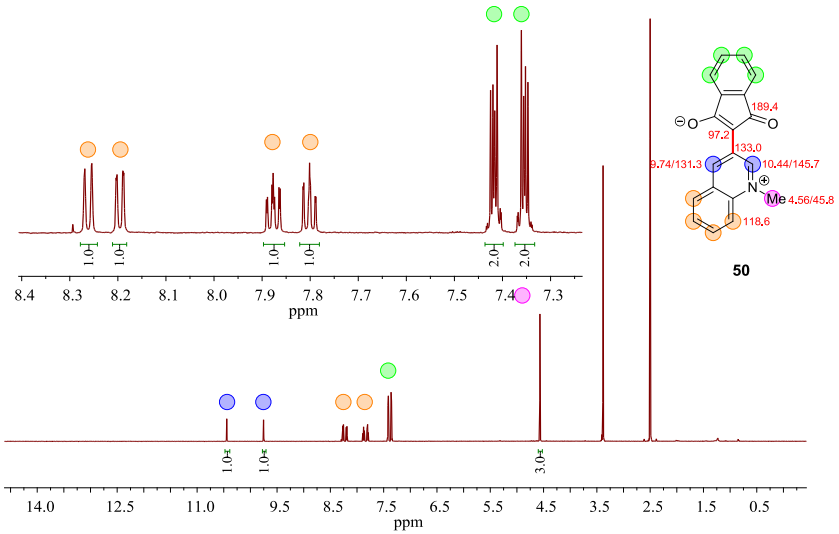
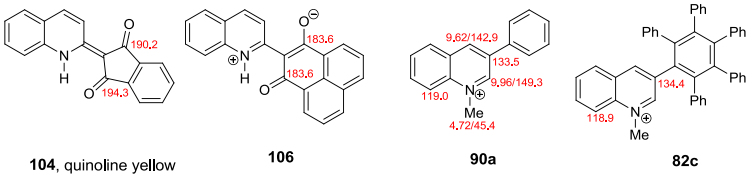


Figure 22: ^{1}H NMR spectrum of betaine **50** in DMSO-d_6 and its characteristic ^{1}H/^{13}C NMR signals

All ^{1}H NMR signals of **50** can be divided into four groups (marked in colored circles). Proton/carbon chemical shifts of NCH_3 (pink) give signals at 4.56/48.8 ppm, respectively, which are comparable to other proton/carbon chemical shifts of quinolinium salts **42a-c** (4.66/4.79/4.64 ppm, respectively). This proves that merely the positive charge is delocalized in the quinolinium ring. Chemical shifts of 2-H and 4-H atoms (blue) lie in the most downfield region of the proton spectrum (10.44, and 9.74 ppm, respectively). They are even more downfield in comparison to 2/4-H hydrogen atoms in 3-substituted quinolinium salts **90a-c** due to intramolecular hydrogen bonding with two carbonyl oxygen atoms. Hydrogens of the fused benzene ring (orange) in quinoline give signals in the region from 8.27 to 7.79 ppm, whereas the corresponding hydrogens in the salts **90a-c** are found in the region from 8.08 to 8.64 ppm. Hydrogens which are not involved in the delocalization of positive and negative charges (green) give two multiplets in the region from 7.42 to 7.35 ppm. The two carbonyl carbon atoms appear as a single signal in the region 189.4 ppm (^{13}C NMR), i. e. here is rotation around the C-C single bond (marked in red) at rt.

It can be seen from these results that betaine 50 displays cross-conjugated behavior in polar solvents. A similar behavior is observed in the neutral compound **106** in chloroform[80] (Scheme 82). Nevertheless, the ^{13}C NMR spectrum of quinoline yellow **104** has two peaks for carbonyl groups with values of 194.3 and 190.2 ppm[80] which most likely shows the planar structure of the molecule under the measuring conditions. As shown before (Scheme 81) molecule **50** is not necessarily twisted to have a higher dipole moment (**50II** or **50II'**), but C-C single bond rotation at rt is an additional evidence of charge separation in polar solutions. Furthermore, the ^{13}C chemical shift of the C3 carbon atom of quinoline has the value of 133.0 ppm which is comparable to the one of the C3 carbon atom in methylquinolinium salt **82c** (134.4 ppm) and the quinoline ring in compound **82c** essentially is not conjugated with an attached substituted phenyl residue. Based on these facts betaine **50** in DMSO has "cross-conjugated" properties.



104, quinoline yellow **106** **90a** **82c**

Scheme 82: Some examples of quinoline derivatives and characteristic $^{1}H/^{13}C$ chemical shifts

Other spectra (Figure 23) of betaine **50** are comparable to the spectrum in DMSO at rt. It also gives the opportunity to assume that betaine **50** is polarized in these solvents and that the electron density of molecule **50** in all presented solvents is comparable (according to chemical shifts).

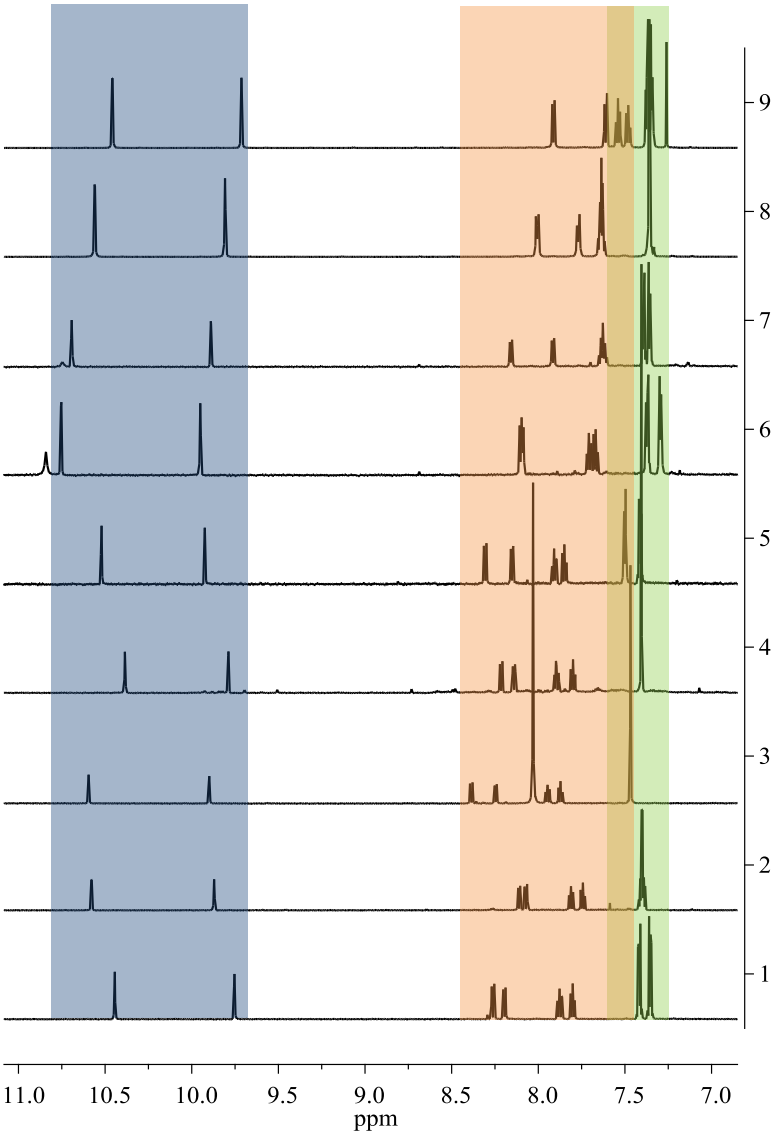
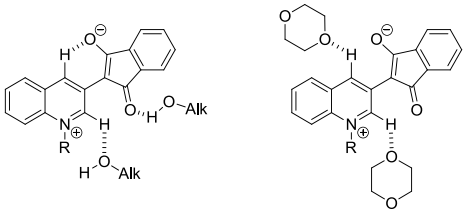


Figure 23: ^{1}H NMR spectrum of betaine **50** in DMSO-d_6 (1), acetonitrile-d_3 (2), DMF-d_7 (3), MeOD-d_4 (4), 2-propanol-d_8 (5), THF-d_8 (6), 1,4-dioxane-d_8 (7), DCM-d_2 (8), and chloroform-d_1 (9)

Signals of NCH_3 hydrogens (not shown in Figure 23) are located in the region from 4.76 ppm in DMF to 4.41 ppm in chloroform.

Analysis of NMR spectra shows five types of different interactions between solvent and solute **50** using the difference between 2-H and 4-H chemical shifts of the quinoline ring as a criterion. E. g., in polar aprotic solvents such as DMSO, DMF, or acetonitrile, the difference of chemical shift between 2-H and 4-H hydrogens is 0.70 ppm. In DCM and chloroform, this difference is 0.75 ppm. In polar protic solvents such as ethanol (not presented in Figure 21 due to solubility), methanol, and 2-propanol the difference is 0.60 ppm, whereas in ethers THF (polar aprotic), and 1,4-dioxane (nonpolar aprotic) is 0.80 ppm. Some possible examples of interaction between solute **50** and solvents are given in Scheme 83:



Scheme 83: Possible interactions between MB **50** and solvents

Betaine **50** is also soluble in benzene and toluene; nevertheless, its ^{1}H NMR spectra are different to the solvents mentioned above. ^{1}H NMR spectrum of **50** in benzene-d_6 is presented in Figure 24. The difference between ^{1}H NMR chemical shifts of 2-H and 4-H hydrogen atoms in benzene is 0.12 ppm, in toluene – 0.20 ppm. This may be due to the lack of hydrogen bonds between solute **50** and solvent (benzene or toluene). Hydrogens which are not involved in delocalization of charges (green color) give signals in the region from 8.01 to 7.20 ppm (benzene) and from 7.88 to 7.20 ppm (toluene). In both cases, hydrogens of the fused benzene ring of quinoline (orange color) shifted upfield in the region from 7.10 to 6.26 ppm in benzene and from 7.10 to 6.35 ppm in toluene. Furthermore, the order of these signals (doublet, triplet, triplet, and doublet) in benzene and toluene are different in comparison to the order in other solvents (doublet, doublet, triplet, and triplet), i. e., the electron density in this ring organized in a distinct way.

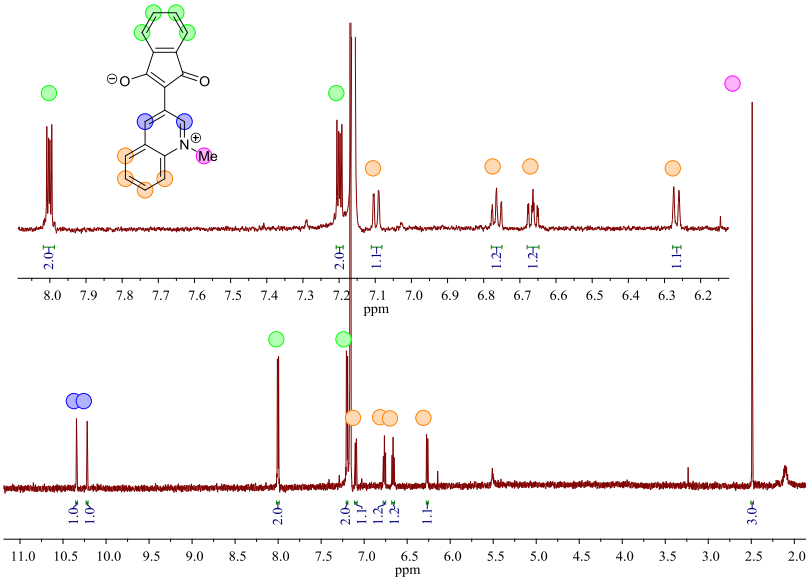
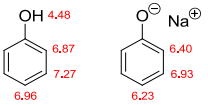


Figure 24: ^{1}H NMR spectrum of betaine **50** in benzene-d_6

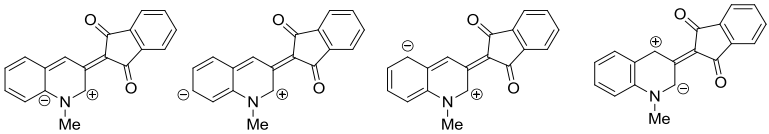
To exclude the possibility of π-stacking between molecules of betaine **50** and benzene the ^{2}H NMR spectrum of **50** was measured. Even after a multiple scaling (512 ×) of benzene ^{2}H spectrum, no other signals were found. Believable, upfield shifts of protons (Figure 24, orange) are a result of the delocalization of the negative charge in quinoline. E. g., in Scheme 84 the difference of ^{1}H chemical shifts between phenol **107**[83] and sodium phenoxide **108**[84] in acetonitrile-d_3 are shown:



Scheme 84: ^{1}H NMR chemical shifts of phenol **107** and sodium phenoxide **108**

Another significant difference is the chemical shift of NCH_3 hydrogens with the values of 2.49 and 2.59 ppm in benzene and toluene, respectively. Likely, mesomeric

structures presented in Scheme 85 have the biggest contribution in the overall picture of the molecule.



Scheme 85: Some mesomeric structures of **50**

In summary, the molecules behave more like conjugated mesomeric betaines in non-polar solvents in comparison to polar solvents.

The HOMO/LUMO profiles of **50** are also given in Figure 25. Due to the small LUMO coefficient on the oxygen atoms and the large LUMO coefficient on C9 carbon atom, it is difficult to see the delocalization of the positive charge on the C9 carbon atom and two oxygen atoms of the indanedione ring which does not contradict the rules of resonance, either. An interesting aspect is the energy level of the HOMO, which is significantly decreased in polar solvents, while the energy level of the LUMO does not change. The HOMO/LUMO gap is 2.61 *in vacuo*, 2.83 in benzene, and 3.13 eV in DMSO. Consequently, MB **50** should show a solvatochromism, what, as a result, was already shown by SMEYANOV[64].

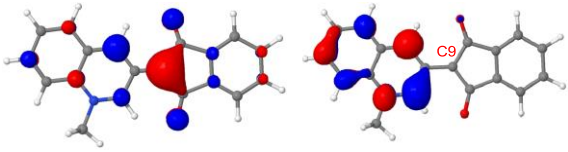
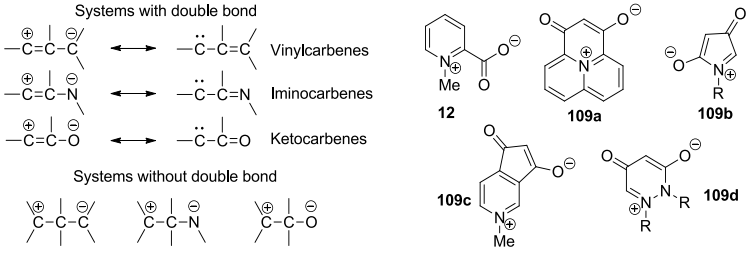


Figure 25: HOMO (left) and LUMO (right) profiles of **50**

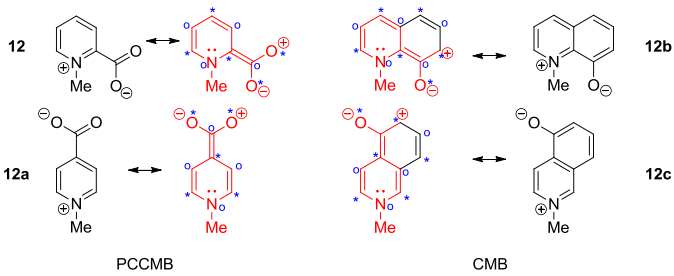
3.4.6 Pseudo-cross-conjugated mesomeric betaines?

In the late 20th century RAMSDEN[23] provided a comprehensive classification of MBs by dividing all betaines into three different classes. In 2013, two more classes were added[36]. In my opinion, RAMSDEN's explanation of the difference between CMBs and PCCMBs has needed clarification. Due to the classification, the only difference is the "*presence of electron sextet structures without electron octet stabilisation*" in the case of PCCMBs, whereas in CMBs all electron sextet structures have internal octet stabilization referring to HUISGEN's[25] classification of 1,3-dipoles (Scheme 86). However, HUISGEN's examples of 1,3-dipoles "*with electron sextet structures without internal electron octet stabilisation*" have electron sextet structures in all mesomeric forms and are considered as non-stable compounds (carbenes or nonconjugated carbocations). In contradiction to the proposed classification rules of MBs, all atoms can be written with eight electrons in the case of PCCMBs, i. e., have internal electron octet stabilization and cannot be distinguished from CMBs.



Scheme 86: The 1,3-dipoles with electron sextet structures without internal octet stabilization by HUISGEN (left) and MBs classified as pseudo-cross-conjugated by RAMSDEN (right)

Other examples of some extensions of Ramsden's original classification are given in Scheme 87. Betaines **12** and **12a** are classified by RAMSDEN as PCCMBs, whereas betaines **12b**, **12c** are CMBs. In the following scheme, the identical segments of the mesomeric structures are marked in red.

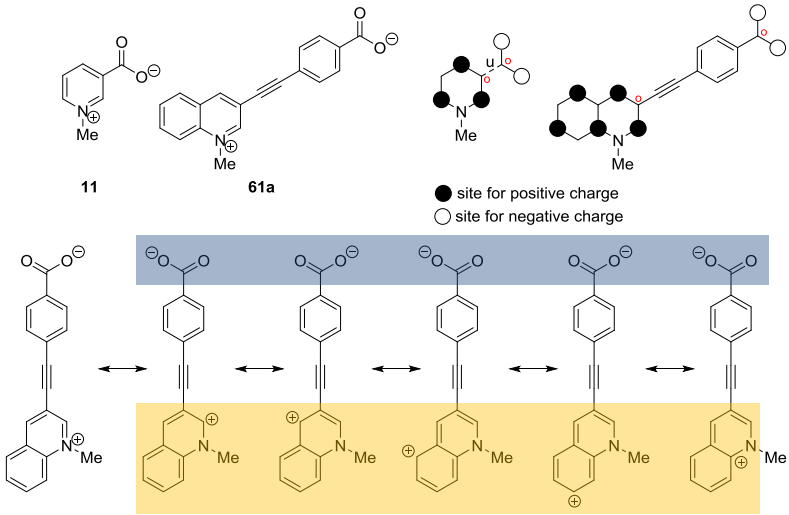


Scheme 87: Comparison of RAMSDEN's PCCMBs and CMBs

Further in this chapter the classification of betaines will be discussed and revised.

- **RAMSDEN's cross-conjugated mesomeric betaines**

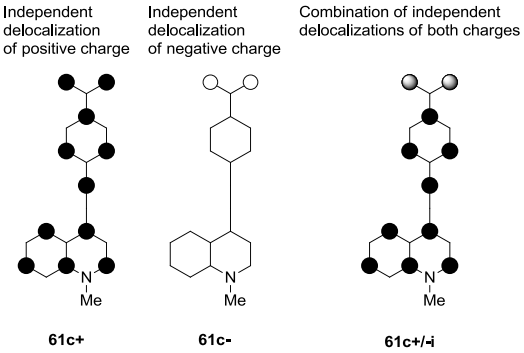
In the case of CCMBs, everything is in accordance: *the positive and negative charges can be shown to be exclusively restricted to separate parts of the π-electron system of the molecule*[23] (Scheme 88).



Scheme 88: CCMBs **11** and **61a** (blue and yellow fields show the parts of betaine in which the positive (yellow field) or the negative (blue field) charges are in classical cross-conjugation)

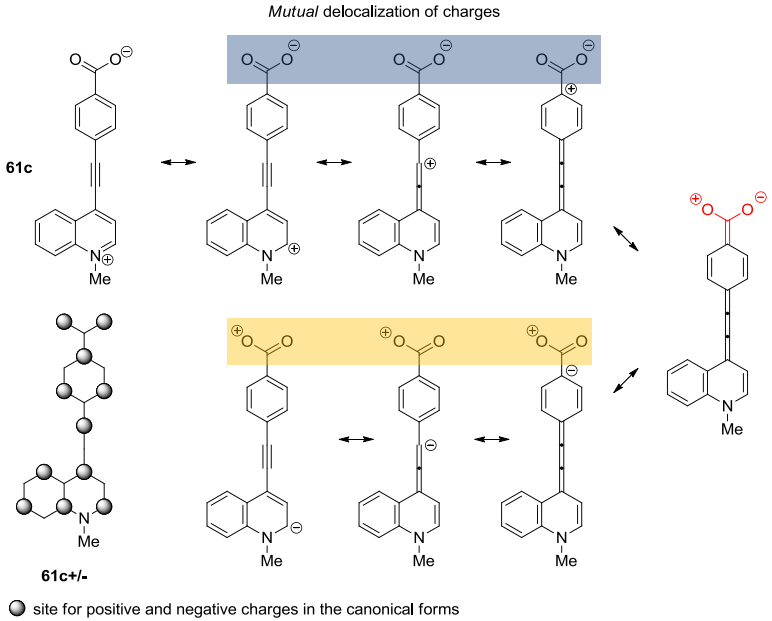
- **RAMSDEN's pseudo-cross-conjugated mesomeric betaines**

Examining the independent charge delocalization of both positive and negative charges within betaine **61c**, it is evident that the positive charge is delocalized in the entire molecule (**61c+**), whereas the negative charge is located on the carboxylic group (**61c-**) (Scheme 89) under the condition that only dipolar resonance forms are taken into consideration according to the aforementioned rules of resonance. The term "independent delocalization" means the delocalization of one charge without the influence of the other.



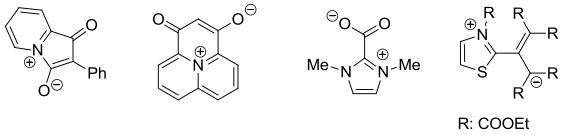
Scheme 89: Charge distribution of the betaine **61c** according to its mesomeric structures

However, *mutual* delocalization of positive and negative charges in molecule **61c** results in **61c+/-** (Scheme 90). The term "mutual delocalization" takes into account that the delocalization of both charges depends on each other. From this point of view, the positive and the negative charges can be delocalized on all same atoms, according to rules of resonance.



Scheme 90: Mutual delocalization of charges in MB **61c** (blue and yellow fields show the parts of betaine in which the positive (yellow field) or the negative (blue field) charges are in classical cross-conjugation)

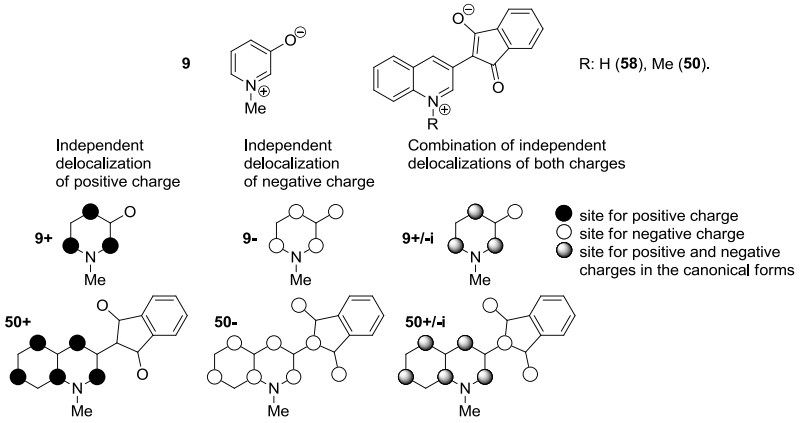
For further verification, different PCCMBs are figured and show the same tendency as well (Scheme 91). The corresponding mesomeric structures of PCCMBs are given in supplementary materials, page 269.



Scheme 91: RAMSDEN's PCCMBs

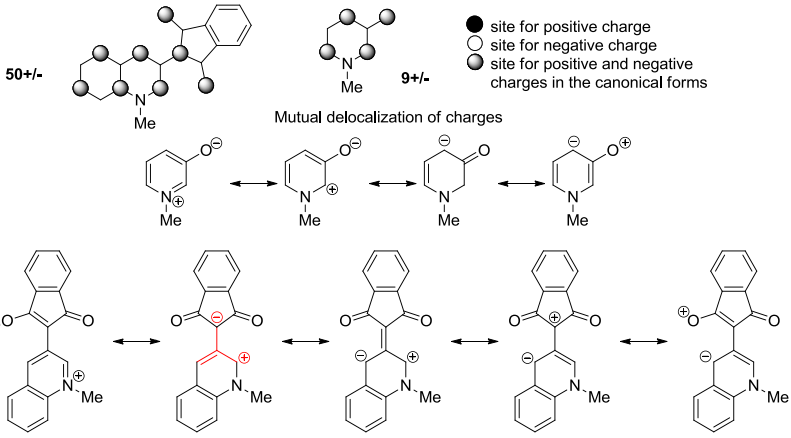
- **RAMSDEN's conjugated mesomeric betaines**

We already reported betaines **50** and **58**, similarly to *N*-methylpyridinium-3-olate **9**, belong to the class of conjugated heterocyclic mesomeric betaines (CMBs)[35] (Scheme 92). The charge contribution of betaine **50**, as well as *N*-methylpyridinium-3-olate **9**, was obtained by a combination of two independent delocalizations of both negative and positive charges in the π-conjugated system and resulted in **58A**, and **9A**, respectively.



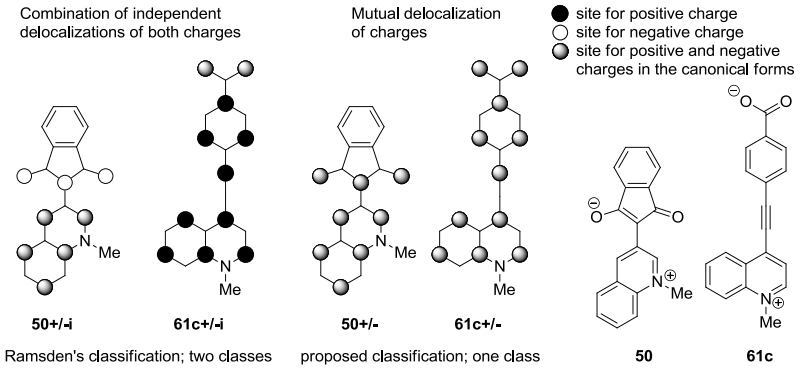
Scheme 92: Conjugated mesomeric betaine **9**, and its π-conjugated analogs **50** and **58**; Charge distribution of betaines **50**, and **9**

However, charges in the molecule are in *mutual* delocalization. Upon closer examination structures **9A**/**50A** proof to be insufficient and should be expanded to structures **9+/-,** and **50+/-** (Scheme 93).



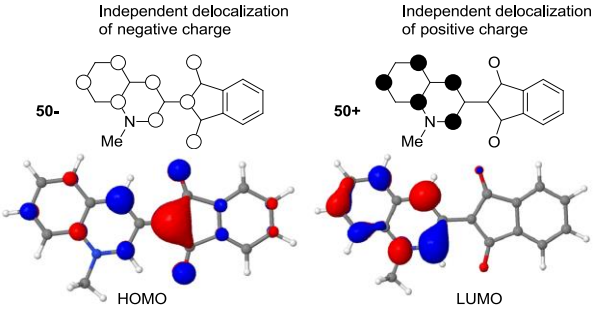
Scheme 93: Mutual charge distribution of the betaines (**9+/-** and **50+/-**) according to their mesomeric structures

As in the previous cases, both positive and negative charges can be delocalized as shown. The charge distributions of betaines **50**, and **61c**, in accordance to their mesomeric structures of *mutual* delocalization, result in the respective figures **50+/-**, and **61c+/-**. These can be obtained in two different ways by a combination of structures **61c+**/**61c-** and **50+**/**50-**. Whereas in so-called PCCMBs the negative charge is delocalized within the entire molecule due to delocalization of the positive charge; in CMBs, it is *vice versa* (Scheme 94).



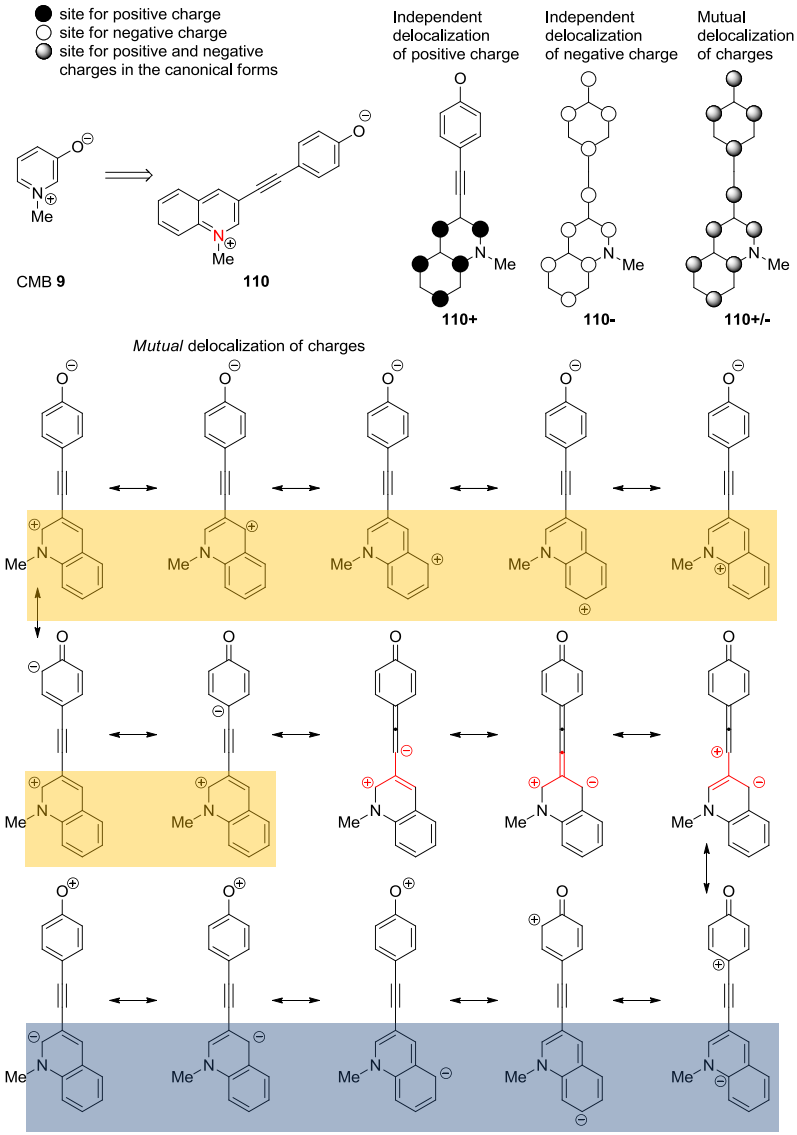
Scheme 94: Comparison of CMB **50** and PCCMB **61c**

By direct comparison of **50**+/-, and **61c**+/-, it is not necessary to differentiate MBs between CMBs and PCCMBs. Betaine **50** is π-extended analog of CMB **9**. Its HOMO/LUMO profiles were discussed in the previous chapter. By inspection of their frontier orbitals and charge distribution **50**+/-, it is difficult to recognize the charge behavior due to small LUMO coefficients as previously mentioned (Scheme 95).



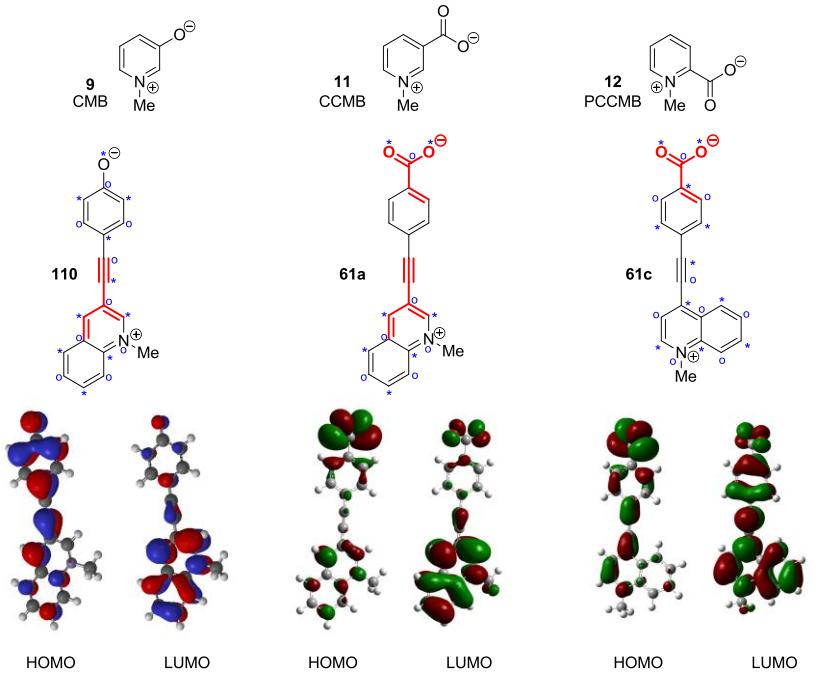
Scheme 95: HOMO (left) and LUMO (right) profiles of **50**

For the better illustration of the proposed theory, an example of a hypothetical CMB **110** is given in Scheme 96.



Scheme 96: CMB **9** and its hypothetical π-extended analog CMB **110**; charge distribution of betaine according to mesomeric structures (blue and yellow fields show the parts of betaine in which the positive (yellow field) or the negative (blue field) charges are in classical cross-conjugation)

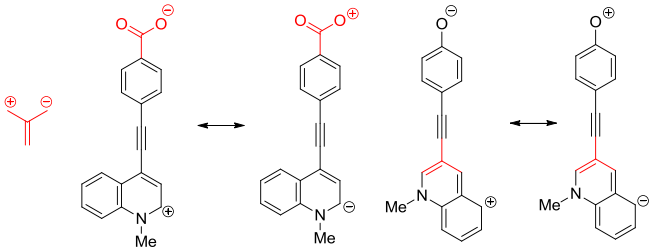
The classical cross-conjugation (as in benzophenone) can elucidate the behavior of charges in the π-conjugated systems. By inspection of the canonical forms of betaines (Schemes 88, 90, 93, 96), it is obvious that the charges are delocalized only in the conjugated part of the molecule. Representatives of three classes of mesomeric betaines by RAMSDEN's classification and their π-extended analogs are displayed in Scheme 97 (cross-conjugated parts marked in red). In MB **110** the quinolinium ring and the triple bond are in cross-conjugation, whereas in MB **61c** the carboxylic group is cross-conjugated with the benzene ring. In CCMB **61a** both cases are present.



Scheme 97: Classical cross-conjugation in CMB **110,** CCMB **61a**, and PCCMB **61c**; the corresponding HOMO/LUMO profiles

As a result, CCMB **61a** has no mutual sites (atoms) for the delocalization of positive and negative charges. Due to cross-conjugation in MB **110**, the positive charge is

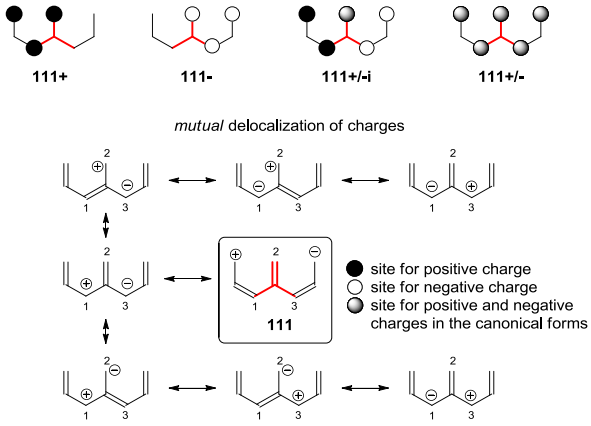
delocalized only within the quinolinium ring. The negative charge is delocalized within the entire molecule. As a result, the positive charge has additional sites of delocalization and consequently, is also delocalized within the entire molecule. In order the compare the electronic situation predicted by the mesomerism, DFT calculations for betaine **110** were performed. The corresponding HOMO/LUMO profiles of **110**, **61a** and **61c** are given in the following scheme. In all three cases, HOMO/LUMO orbitals are located on the atoms on which the positive or negative charges are delocalized according to the mesomeric structures. The delocalization of the negative charge in betaine **61c** on the entire molecule is possible due to the four-atomic system ϒ (Scheme 98, marked in red), in which the positive and negative charges can be exchanged. The same system is present in betaine **110** because the positive charge is delocalized not only on the quinolinium ring but on the entire molecule as well. The direct comparison of the HOMO/LUMO profiles of MBs **61c** and **110** likely shows that both betaines belong to one same class. Comparing the mesomeric structures of Ramsden's PCCMB **61c** and CMB **110**, the delocalization of charges in both betaines is identical. The positive and the negative charges are in cross-conjugation in the classical sense (as in benzophenone) which induced a π-electronic charge separation, respectively, between two parts of the molecule unless the polarity changes from plus to minus and *vice versa* when the increment ϒ is developed and a new set of resonance forms can be written starting from ϒ (Scheme 98).



61c **110**

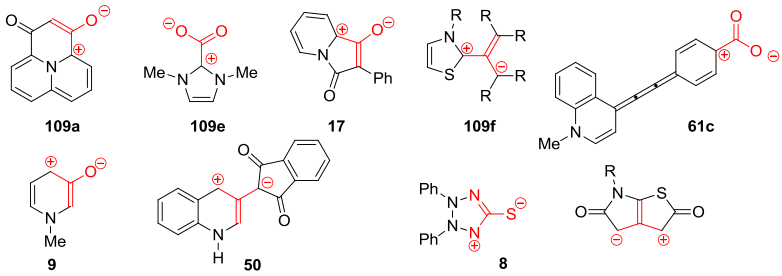
Scheme 98: Charge behavior in MBs **61c** and **110**

Possibly, CMB **110** is a more stable compound compared to PCCMB **61c** because of the "*internal octet stabilisation*" by the nitrogen atom (positive charge on the nitrogen atom). Likely, STANFORTH, OLLIS, and RAMSDEN considered this as a difference between MBs, such as **61c** and **110**, and created the class PCCMB. However, to my opinion, delocalization of positive charge results in octet stabilization. In mesomeric betaines without the corresponding stabilizing heteroatom, the originally distinct classes of CMBs and PCCMBs have been regarded as identical. The hypothetical betaine **111** is as an example. In the betaine **111**, both the positive and negative charge can be located at the site (2), and as a result at all other sites too (Scheme 99). I. e., in CMBs as well as in PCCMBs at each starred position the positive or negative charge can be delocalized by overcoming the classical cross-conjugation. Hence, MB **111** cannot be classified as either CMB or PCCMB in the sense of OLLIS, STANFORTH, and RAMSDEN.



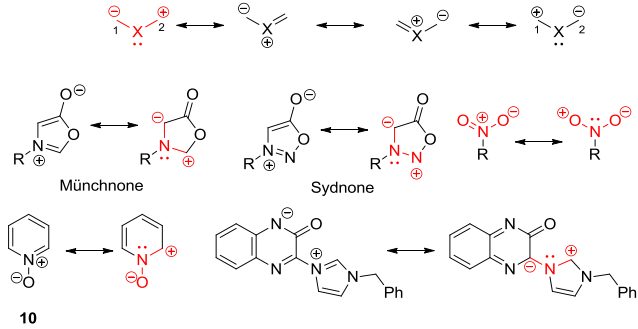
Scheme 99: Hypothetical MB **111**: **111+** independent delocalization of the positive charge, **111-** independent delocalization of the negative charge, **111+/-i** combination of **111+** and **111-**, and **111+/-** dependent delocalization of charges

Few examples of MBs are presented in Scheme 100, in which the aforementioned four-atomic system is marked in red.



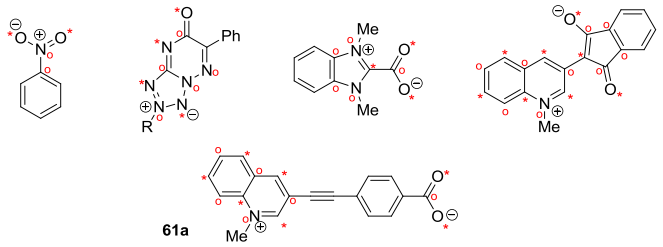
Scheme 100: PCCMBs (above) and CMBs (below)

This four-atomic system **Y** is not present in all MBs and the "exchange" of charges is possible due to the lone pair on heteroatoms. Such examples of MBs are sydnones, münchnones, or ylides also given in Scheme 101.



Scheme 101: The "exchange" of charges in sydnones, münchnones, and ylides

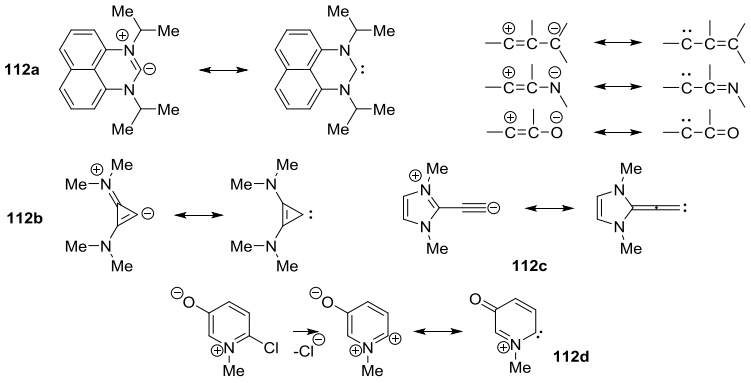
In *conjugated* and *cross-conjugated* mesomeric betaines the charges are delocalized within the conjugated system. However, in some MBs charges cannot be delocalized in certain parts of the molecule due to classical cross-conjugation (Scheme 102).



Scheme 102: Examples of betaines in which the charges are not delocalized on the entire molecule

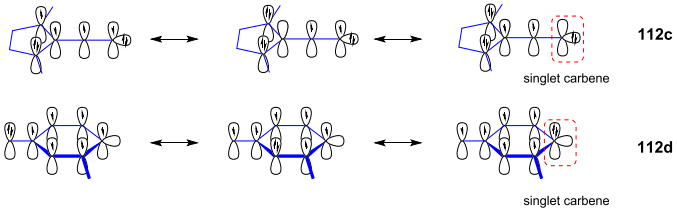
However, the properties of MBs are dependent on the nature of atoms (C, N, O …), chemical structure (main skeleton, substituents) as well as the influence of solvents, other neighboring molecules, and temperature, or other physical factors.

Not all betaines were included in RAMSDEN's classification. In the betaines in this chapter above, the positive, as well as the negative charges, are included in one π-conjugated system, i. e., the charges are shared in the same π-orbitals, which are parallel or almost parallel to each other. As a result, one starred atom can carry only one charge (positive or negative), and not two charges at once. Whenever the positive and the negative charges do not share any parallel orbital, these betaines are in mesomerism to their corresponding carbenes (Scheme 103).



Scheme 103: Examples of carbene/betaine mesomerism

In cases of carbenes **112a-c**, the negative charge is in a fixed carbon atom, while the positive charge is delocalized in π-conjugated system. In HUISGEN's 1,3-dipoles, as well as in proposed hypothetical carbene **112d** the position (the C6 carbon) of the positive charge is fixed, whereas the negative charge is delocalized. As a result, the formed singlet carbene in **112a-c** differs to the singlet carbene in **112d** (Scheme 104).

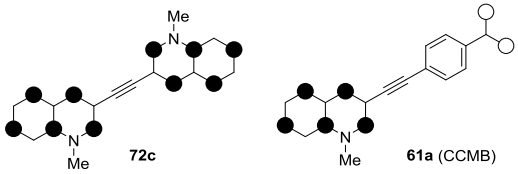


Scheme 104: Comparison of singlet carbenes **112c** and **112d**

3.4.7 Classification of mesomeric dicationic salts

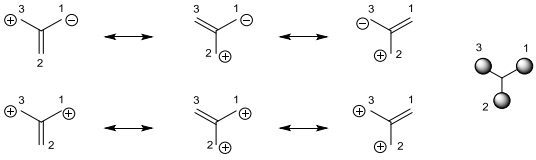
Based on the revised classification of MBs in the previous chapter, additional bicharged systems - heterocyclic mesomeric dicationic salts - were classified. Whereas in betaines two charges are located within one molecule, the counterions of salts can have an additional influence on molecule properties. In agreement to the proposed classification, salts show different properties.

In compound **72c** two positive charges are in cross-conjugation and do not delocalize into the C≡C triple bond, as the two quinoline rings are in cross-conjugation to the C≡C triple bond (Scheme 105). In analogy to the classification of MBs, the salt **72c** is classified as *cross-conjugated*.



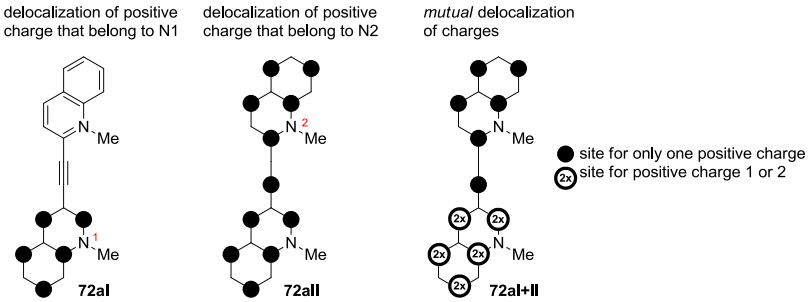
Scheme 105: CCMB **61a** and *cross-conjugated* dicationic salt **72c**

As mentioned before, in my opinion there is no difference between CMBs and PCCMBs, and the properties of both classes of betaines merely differ according to the rules of resonance. In CMBs or PCCMBs, the delocalization of both positive and negative charges leads to a charge distribution across the entire molecule. Similar to conjugated mesomeric betaines, the overcoming of classical cross-conjugation is realized in the four-atomic system as well (Scheme 106). As a result, in conjugated dicationic salts the charges are distributed across the entire molecule as well.



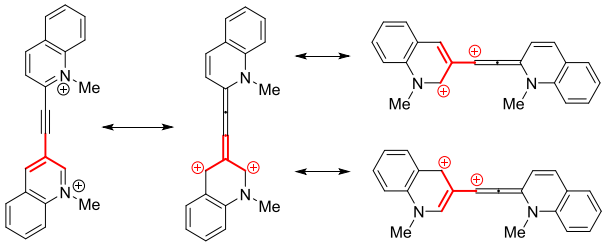
Scheme 106: Bypassing of classical cross-conjugation in CMBs and conjugated mesomeric dicationic salts

In case of conjugated salts using the terms “conjugated” or “pseudo-cross-conjugated” can be used equally due to two identical charges in the conjugated cationic parts of the mentioned salts. The salts **72a**, **b** can be classified as *conjugated* dicationic salts. The charge distribution according to mesomeric structures of **72a** is shown in Scheme 107.



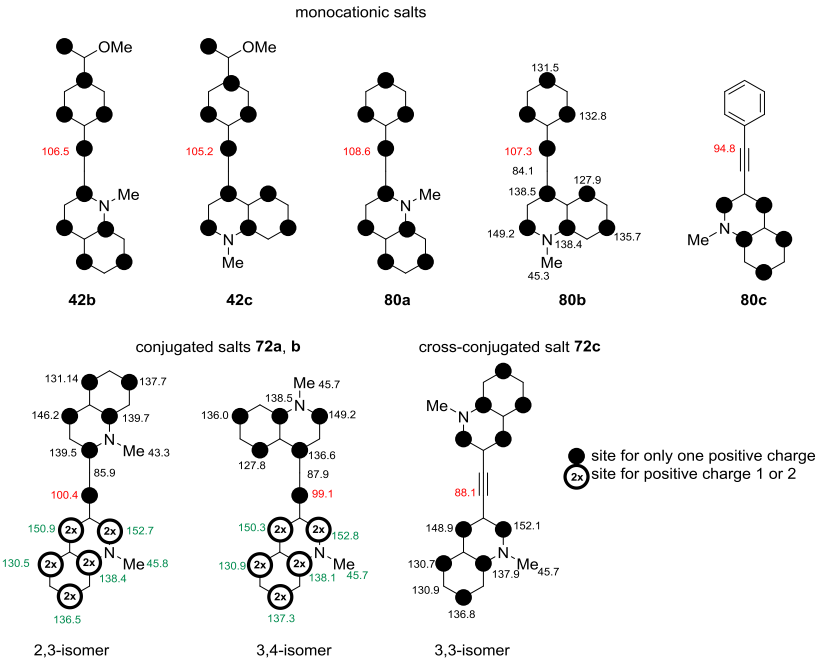
Scheme 107: Charge distribution according to mesomeric structures of *conjugated* salt **72a**

In addition, the inspection of mesomeric structures of **72a** shows, that the delocalization of two identical (positive) charges resulted in the distribution of one positive charge in the entire molecule and another one just partially (Scheme 108). The delocalization of two charges is possible in quinolinium-3-yl residue, whereas only one charge can be delocalized on the triple bond and quinolinium-2-yl residue. The four-atomic system is marked in red.



Scheme 108: Some mesomeric structures of **72a**

The proposed theory for the classification of compounds **72a-c** is supported by NMR spectroscopy (Scheme 109).

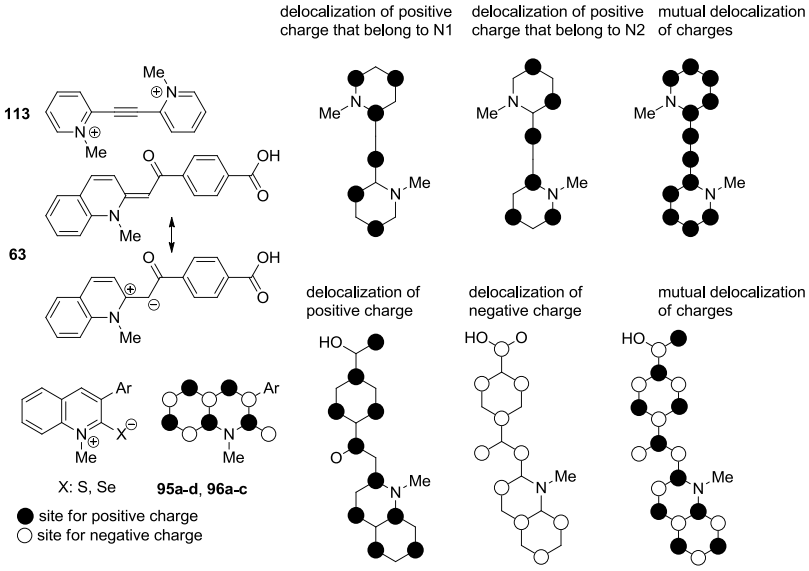


Scheme 109: *Cross-conjugated* salt **72c**, *conjugated* **72a**, **b**; Monocationic salts **42b**, **c**, **80a-c**; characteristic ^{13}C NMR chemical shifts of salts

The ^{13}C NMR chemical shifts of **72c** (*cross-conjugated* salt) differ from the other two isomers **72a**, **b** and are comparable to the similarly structured salt **80c**, in which the positive charge is delocalized only in the quinolinium moiety. Comparing the chemical shifts of the carbons in the monocationic salts **42b**, **c**, and **80a**, **b** to *conjugated* dicationic salts **72a**, **b** it becomes evident that the C≡C carbon atom shifts are most characteristic (marked in red). In the monocationic salts **42b**, **c** and **80a**, **b** the chemical shifts of the carbon Cβ is in the range from 105 to 109 ppm. In the salts **72a**, **b**, the signal of the Cβ carbon atom has values of 100.4 and 99.1 ppm, respectively. Likely, this is a result of delocalization of the positive charge on more carbon atoms in the salts

72a, **b** in comparison to the monocationic salts **42b**, **c** and **80a**, **b**. In addition, the carbon shifts of methylquinolinium-3-yl residues (marked in green) in **72a**, **b** are slightly shifted downfield compared to other methylquinolinium carbon shifts.

One additional class was recognized by the analysis of mesomeric structures of dicationic salts, in which the two positive charges are delocalized on two neighboring atoms. An example is compound **113** which has been synthesized by HAINDL[85] (Scheme 110). In compound **113** each carbon atom of the π-conjugated system can carry the positive charge because compound **113** is classified as *fully-conjugated*. "Fully conjugated" means that all atoms are possible sites for positive charges as shown. In the classification of betaines, analogous compounds do not exist. If the negative and positive charges are located on two neighboring atoms, they can form a normal chemical bond. Therefore, compound **63** and similar compounds (**103, 105, 95a-d, 96a-c**) are neutral and not classified as betaines.



Scheme 110: Compound **113** synthesized by HAINDL; neutral compounds **63**, **95a-d**, and **96a-c**

The dicationic compounds **77a-d** are π-extended analogs of the previously mentioned compounds and can be classified in the same way: **77c** is *cross-conjugated*, **77d**, **e** are *conjugated*, and **77a**, **b** are *fully-conjugated*. Minimum structure calculations of compounds **77a**, **c**, **d** show that all three isomers are planar and two methyl groups in each of them are in *trans* conformation (Figure 26).

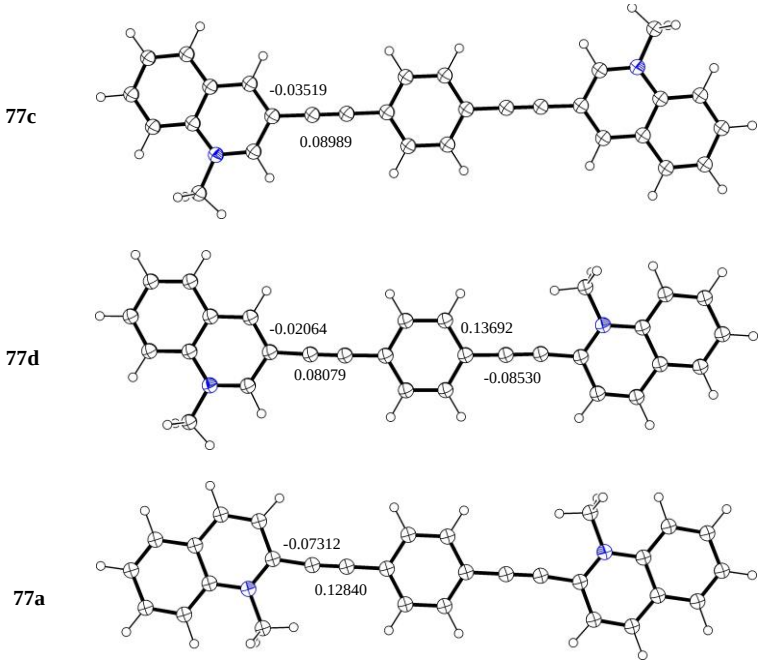
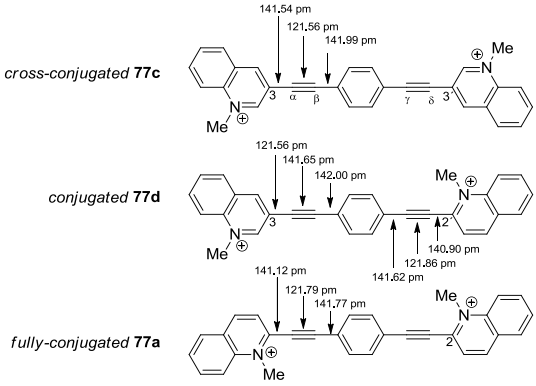


Figure 26: True minimum structures of dicationic salts **77a**, **c**, **d**; calculated partial charges atoms of C≡C triple bonds

In the *cross-conjugated* compound **77c** the calculated C≡C triple bond length is 121.56 pm, neighbored C3-Cα and C1″–Cβ single bond lengths are 141.54 and 141.99 pm, respectively (Scheme 111). In the *conjugated* compound **77d** the Cα≡Cβ triple bond is only very slightly shorter (121.53 pm) compared to the corresponding C≡C triple bond in **77c**. The neighbored C3-Cα and C1″-Cβ single bond lengths are slightly longer (141.65 and 142.00 pm, respectively). The calculated Cγ≡Cδ triple bond

length is 121.86 pm; the C4″–Cγ and Cδ–C3′ single bond lengths are 141.62 and 140.90 pm, respectively. In dicationic salt **77a** the corresponding bond lengths are 121.79, 141.12, and 141.77 pm for Cα≡Cβ, C2-Cα, and C1″-Cβ, respectively. Shorter C≡C triple bond lengths in **77c** can be explained by the absence of cumulenoid mesomeric structures similar to the salt **42a** discussed in previous chapters. It also reflected in the C≡C triple bond absorption values in the corresponding IR spectra: 2219 cm^{-1} for **77c**, 2203 and 2200 cm^{-1} for **77a**, and **77d**, respectively.



Scheme 111: Calculated characteristic bond lengths of dicationic salts **77a**, **c**, **d**

The calculated HOMO/LUMO profiles also support the proposed classification. In the same manner as in salts **42a-c** the LUMO profiles of **77a**, **c**, **d** clearly describe the delocalization of two positive charges in conjugated systems obtained from their mesomeric structures. Figure 27 shows the charge distributions of dicationic salts **77a**, **c**, **d** according to their mesomeric structures.

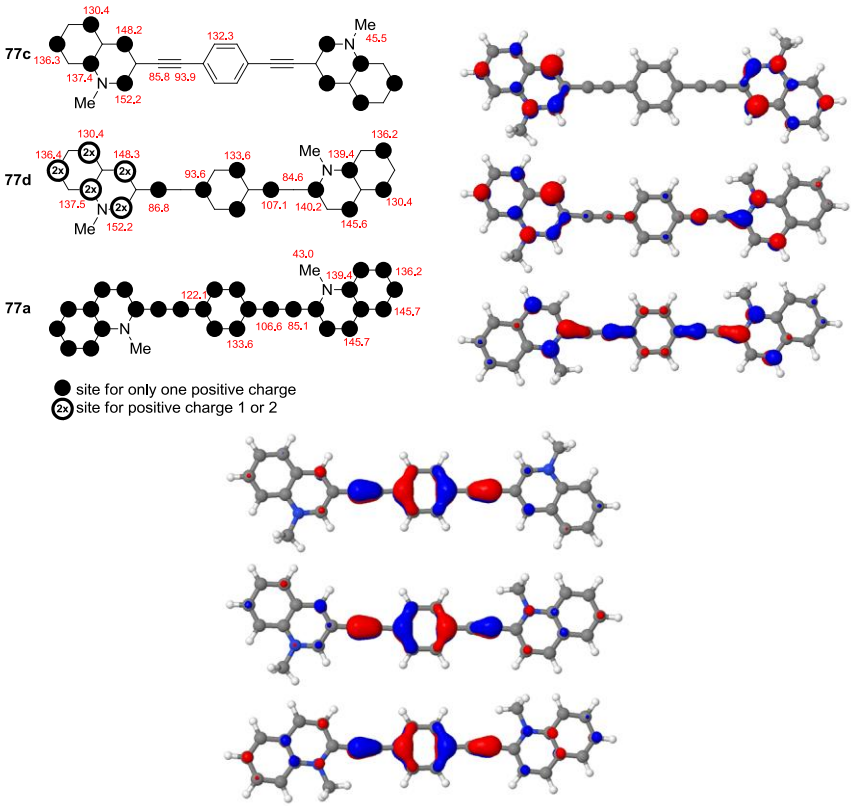


Figure 27: Charge distribution according to mesomeric structures of **77a**, **c**, **d** and their LUMO (right) and HOMO (middle) profiles; Characteristic ^{13}C NMR signals marked in red

Furthermore, these charge distributions are compared to the LUMO profiles of the aforementioned salts. In all three cases, the LUMO coefficients of fused phenyl rings are smaller than the analogous one in the pyridine ring satisfying the rules of resonance. HOMO profiles in all three cases are comparable and carry the highest coefficients on the C≡C triple bonds and the central phenyl ring.

3.4.8 UV/Vis spectra of diquinoline derivatives and TDDFT calculations

For further approvement, UV/Vis spectra were measured for the neutral compounds (**71a-c**, **76a-e)** and their corresponding *N*-methylquinolinium salts (**72a-c**, **77a-e** and dihexafluorophosphate analogs) in three different solvents, i. e., methanol (1.70 D), acetone (2.88 D), and acetonitrile (3.92 D) in the range from 280 to 800 nm at rt (20 °C). The UV/Vis spectra of the neutral compounds **71a-c** are similar in all three solvents. Compound **71a** gives an absorption peak of 347 nm, **71b** – 349.5 nm, and **71c** – 345.5 nm. In Figure 28 UV/Vis spectra of neutral compounds **71a-c** in acetonitrile including main absorption peaks are presented.

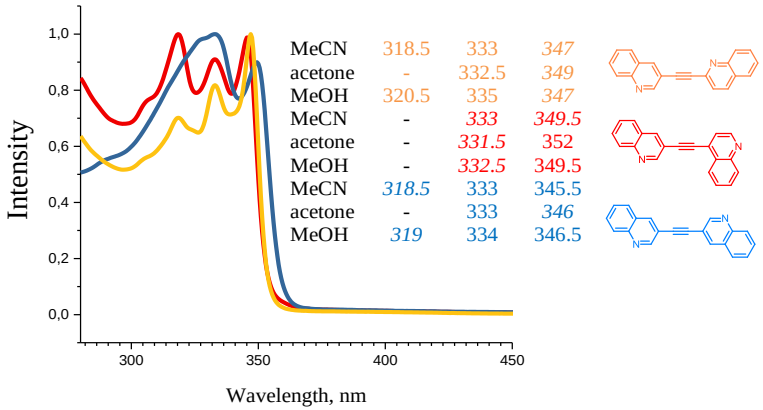


Figure 28: UV/Vis spectra of neutral compounds **71a-c** in acetonitrile including absorption peaks of UV/Vis spectra in three solvents (most intensive peaks marked in italics)

The neutral π-extended compounds **76a-e** do not differ significantly (Figure 29). In addition, the neutral compounds **71a-c** do not absorb beyond 370 nm, the π-extended analogs **76a-e** – beyond 385 nm and further absorption peaks can be observed in the region of 360-370 nm.

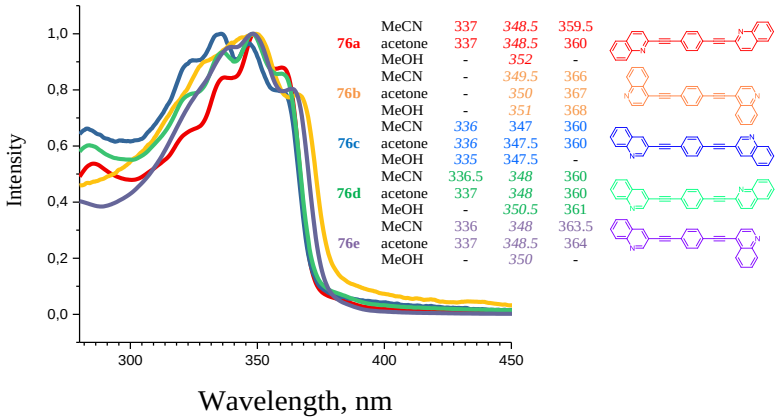


Figure 29: UV/Vis spectra of neutral **76a-e** in acetonitrile; absorption peaks of UV/Vis spectra in three solvents (most intensive peaks marked in italics)

In contrast, UV/Vis spectra of the dicationic salts **72a-c** differ from each other (Figure 30). Depending on the solvent used, *conjugated* salts (**72a**, **b**) have absorption peaks in the range from 480 to 510 nm, whereas *cross-conjugated* **72c** have those from 410 to 430 nm.

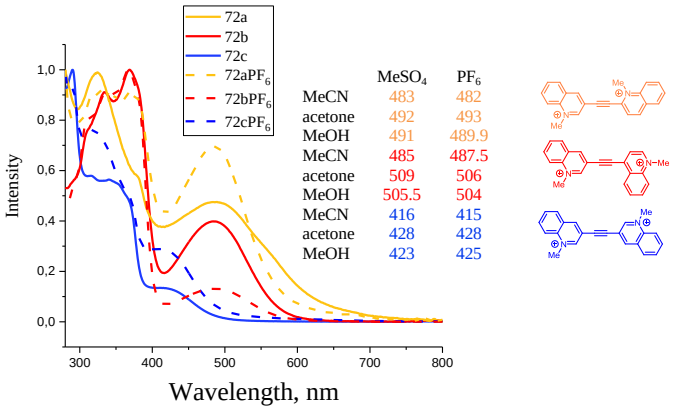


Figure 30: UV/Vis spectra of methylsulfate (**72a-c)** and hexafluorophosphate salts (**72aPF$_6$-cPF$_6$**) in acetonitrile and their absorption peaks in three solvents

Absorption peaks of dicationic dihexafluorophosphate salts **72aPF$_6$-cPF$_6$** are compatible to the dimethylsulfate salts **72a-c**. The π-extended dicationic salts **77a-e** as well as their dihexafluorophosphate analogs also differ from each other (Figure 31). *Cross-conjugated* salt **77c** gives an absorption peak of 369 nm in acetonitrile, *conjugated* salts **77d**, **e** – 394 nm, and *fully-conjugated* salts **77a**, **b** – 408 nm, which nicely support the proposed theory about delocalization of charges – absorption peaks are similar to the same class and differ from other classes.

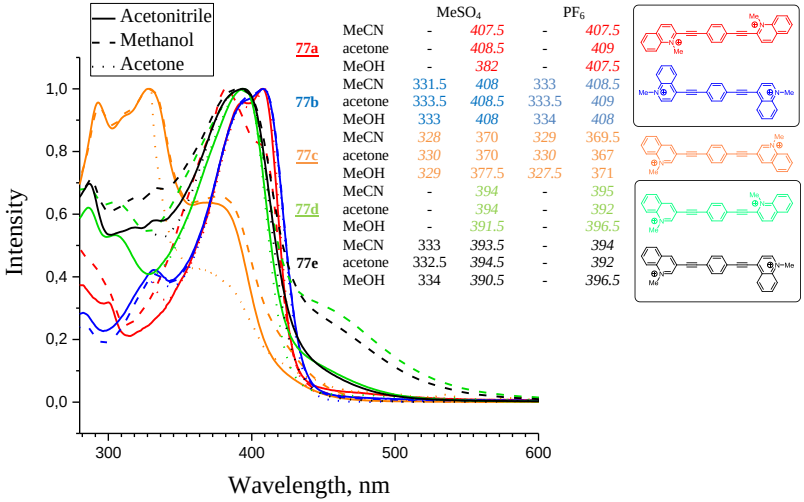


Figure 31: UV/Vis spectra of methylsulfate salts **77a-e** in three solvents including absorption peaks of **77a-e** and their hexafluorophosphate analog in three solvents (most intensive peaks marked in italics)

Calculations of UV/Vis spectra for three different classes of dicationic salts were performed. As representatives of three classes of dicationic salts, the compounds **77a**, **c**, **d** were chosen. Calculations do not include the influence of solvents, which will have an impact with increasing polarity. The UV transitions (wavelength, nm) and the intensities (oscillator strength) are given in Table 56 (c.f. supplementary). The first 12 transitions for the three compounds have been calculated. UV transitions with significant oscillator strengths are relevant; all other transitions are forbidden and not

visible in the measured spectra. In case of *fully-conjugated* salt **77a** only the first transition is intense (osc. str. = 2.80), other transitions are smaller (osc. str. ≤ 0.073). The first transition (410 nm) is caused by an excitation from HOMO to LUMO: it is a pure and allowed HOMO - LUMO excitation (Figure 32) and close to measured spectra in acetonitrile (407.5/407.5 nm; $MeSO_4/PF_6$), and acetone (408.5/409 nm; $MeSO_4/PF_6$), whereas in methanol the absorption maximum likely depends on anion nature (382/407.5 nm; $MeSO_4/PF_6$).

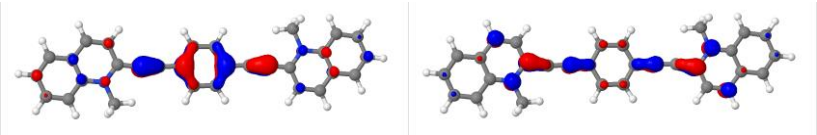


Figure 32: HOMO (left) and LUMO (right) frontier orbitals *fully-conjugated* **77a**

In the case of the *conjugated* salt **77d**, calculations do not show only one, but several allowed transitions. The first one at 419.50 nm (osc. str. = 1.36), the second one at 392.40 nm (osc. str. = 0.95), and some weaker ones at 321.96 (osc. str. = 0.21), 314.79 (osc. str. = 0.33), and 292.08 (osc. str. = 0.39) nm, respectively. The first transition at 419.50 nm is the HOMO - LUMO excitation and the second transition at 392.40 nm is the HOMO - LUMO+1 excitation. The corresponding frontier orbitals are given in Figure 33.

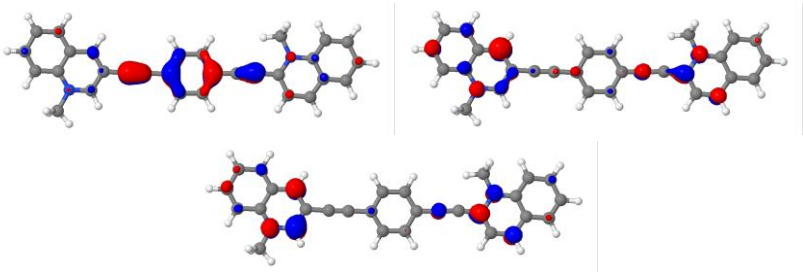


Figure 33: HOMO (left), LUMO (right) and LUMO+1 (middle) frontier orbitals of *conjugated* **77d**

According to the TDDFT calculation, the measured absorption peak in the range from 392 to 396 nm, depending on solvents and anions, is the HOMO-LUMO+1 excitation.

Calculations of the *cross-conjugated* salt **77c** give two transitions at 445.70 nm (osc. str. = 0.64) and 351.24 nm (osc. str. = 2.16). The first transition at 445.70 nm is the HOMO – LUMO excitation, and the second, which is more intense, at 351.24 nm is the HOMO – LUMO+2 excitation. The corresponding frontier orbitals are given in the following figure.

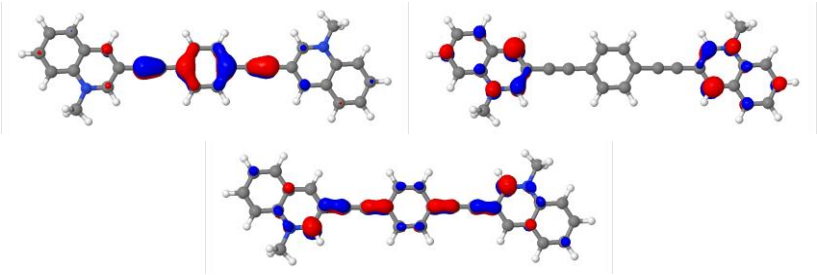


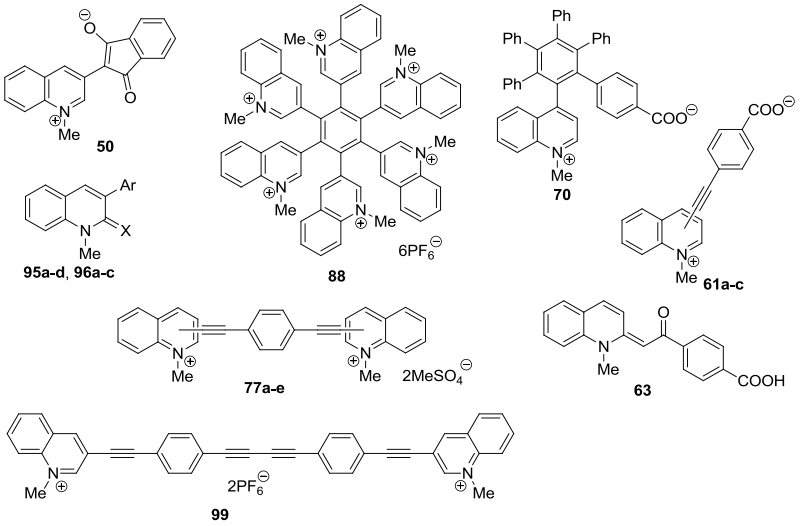
Figure 34: HOMO (left), LUMO (right) and LUMO+2 (middle) frontier orbitals of *cross-conjugated* **77c**

The measured UV/Vis spectra of **77c** do not give absorption peaks at the region around 445 nm, and absorption peaks in the range from 367 to 371 nm likely is the HOMO - LUMO+2 excitation.

Considering that the calculated UV spectra were performed *in vacuo* and an absolute "error" in theory about 20-40 nm compared to the experiment is common for TDDFT, calculated spectra show the correct tendency with experimental data and support the proposed classification.

4. SUMMARY AND CONCLUSIONS

In this work, different quinoline derivatives were synthesized (Scheme 112). Furthermore, the analysis of the obtained information led to an adjustment of the classification of mesomeric betaines.

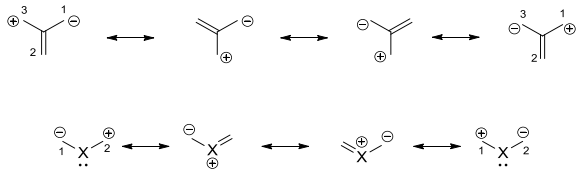


Scheme 112: Various examples of methyl quinolinium derivatives

The synthesis of π-conjugated methyl quinolinium salts **42a-c**, with further analysis, showed the difference between betaine precursors. DFT calculations of the corresponding betaines **61a-c** helped to elucidate the behavior of both positive and negative charges in π-conjugated systems. The HOMO/LUMO profiles of betaines **61a-c** are in good agreement with their mesomeric structures. The information gained might enable the classification of other betaines as well.

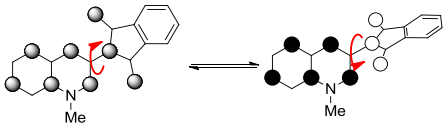
The classification of mesomeric betaines was revised and modified. It was shown that pseudo-cross-conjugated mesomeric betaines do not differ to conjugated mesomeric betaines and theoretically belong to a single class of betaines. The difference is

conditioned only by nature of atoms carrying the positive or negative charges, and whose charge actually is in cross-conjugation to a conjugated system. The temperature or type of solvents has an influence as well. Moreover, it was demonstrated how two charges can be exchanged in a conjugated system in CMBs eluding cross-conjugation (Scheme 113).



Scheme 113: Mechanisms of charge exchange in conjugated bicharged compounds

According to the postulated classification heterocyclic mesomeric betaines as well as mesomeric betaines in general, can be divided into two major classes: conjugated and cross-conjugated. It was shown that the term "pseudo-cross-conjugated" is not appropriate, and some properties (bond lengths, solubility, stability) of betaines were explained. In addition, it has been shown that the properties of betaines also depend on its skeleton. Furthermore, it has been shown that the change in dihedral angles can impact a betaine's classification (Scheme 114).



Scheme 114: CMB-CCMB dihedral angle interconversions of **50**

NMR experiments with conjugated mesomeric betaine **50** have shown the possibility to change the class of CMBs by replacing the solvent (Figure 35). It was shown that MB **50** is twisted in DMSO at rt and *per definitionem* classified as CMB, whereas *de facto* it is CCMB.

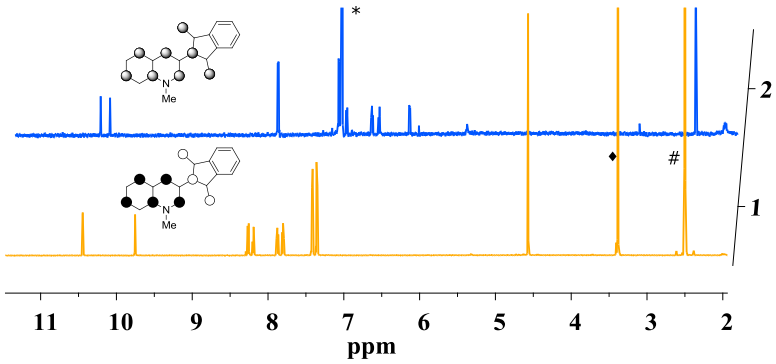
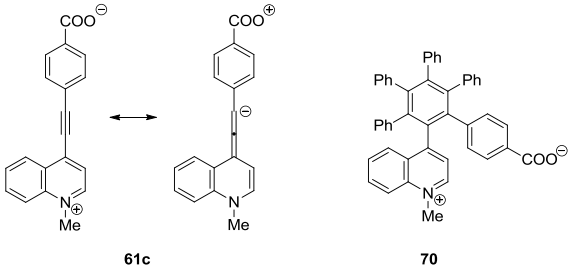


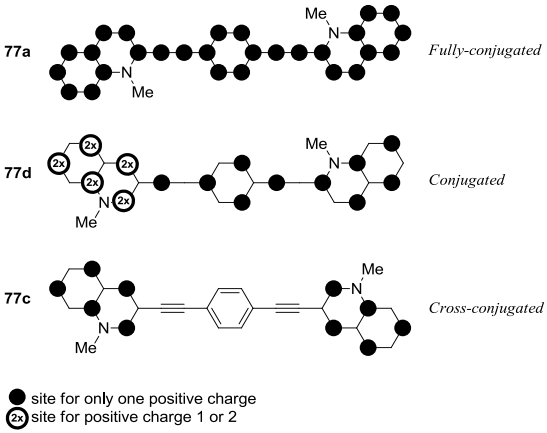
Figure 35: ^{1}H NMR spectrum of betaine **50** in benzene-d_6 (top) and DMSO-d_6 (bottom); *-benzene d_6, #-DMSO d_6, ♦-water.

The synthesis of non-stable betaines **61b**, **c** in comparison to the formation of the stable MB **70** showed the impact of dihedral angles in the properties of betaines as well as their classification (Scheme 115).



Scheme 115: Non-stable betaine **61c** and betaine **70**

The classification was also extrapolated on another bicharged system – mesomeric dicationic salts – which shows a good tendency of the proposed classification. In the case of dicationic salts one more class was recognized (Scheme 116).



Scheme 116: Representatives of three classes of mesomeric dicationic salts

IR, ^{13}C NMR, and UV/Vis spectra as well as calculations of true minimum structures, and TDDFT calculations supported the proposed classification. Comparison of calculated UV/Vis spectra with experimental ones shows that in measured spectra of *fully-conjugated* salt **77a** the absorption peak at 407.7 nm (acetonitrile) is the HOMO - LUMO excitation, *conjugated* **77d** at 394 nm - HOMO – LUMO+1 excitation, and *cross-conjugated* **77c** at 370 nm - HOMO - LUMO+2 excitation. This gives the possibility of syntheses of new dicationic salts with promising properties. In addition, it is likely that the proposed classification can be used for mesomeric dianionic salts as well.

Synthesis of 3-aryl substituted salts **90a-c**, **82c** with further trapping reactions with sulfur and selenium gives the opportunity of using quinolinium salts as carbene precursors. A mechanism for the trapping reaction was proposed.

5. EXPERIMENTAL SECTION

5.1 General considerations

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage.

Melting points: Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi).

ATR-IR Spectra: The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1}.

^{1}H NMR-Spectra: ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz.

^{13}C NMR-Spectra: ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2).

^{77}Se NMR-Spectra: ^{77}Se NMR spectra were recorded at 114 MHz.

^{31}P NMR-Spectra: ^{31}P NMR spectra were recorded at 243 MHz.

Mass spectra: The electrospray ionization mass spectra (ESIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS (EIMS) or with an Agilent LCMSD series HP 1100 with APIES at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V unless otherwise noted.

High-resolution mass: The HR-MS spectra were obtained with a Bruker Impact II, a Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer, or with a Waters Micromass LCT with the direct inlet.

Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F_{254}, company MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230-400 mesh) of the company MERCK KGAA.

Crystal Structure Determination: The single-crystal X-ray diffraction studies were carried out at 123(2) K using Mo Kα radiation (λ = 0.71073 Å) (**42a**, **43PF$_6$**) or Cu Kα radiation (λ =1.54178 Å) (**48PF$_6$**, **50×HCl**, **95b**, **96c**). Direct methods (SHELXS-97)[86] or dual space methods (**50×HCl**) (SHELXD)[86] were used for structure solution, and refinement was carried out using SHELXL-2014 (full-matrix least squares on F2).[87] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(O) free). Semiempirical absorption corrections were applied. For **43PF$_6$** and **48PF$_6$**, extinction corrections were applied.

DFT-Calculation: Density-functional theory (DFT) calculations were carried out using the Jaguar 8.3.012 software[88] running on Linux 2.6.18-238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI. MM2-optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay−Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using Maestro 9.7.012, the graphical interface of Jaguar. Solvent effects were estimated by the help of the Poisson−Boltzmann Finite element method implemented in Jaguar. Partial charges were obtained with NBO 6.0[89] from the results of the DFT calculations.

The experimental Raman spectra salts **42a-c** were conducted in comparison to the calculated ones, using a 6-311g(d,p) basis set, within the frame of the DFT theory at the b3lyp level.

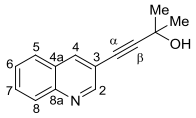
For dicationic salts **77a**, **c**, **d** and eight rotamers of **88** density-functional theory (DFT) calculations were carried out using the Firefly 8.2.0 QC package[90], which is partially based on the GAMESS (US)[91] source code, with Infiniband interconnect and parallelized with MPICH 1.2.7p1.
MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented N31G6* basis set and with the PBE0 density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. UV/Vis transitions for dicationic salts **77a**, **c**, **d** were obtained by time-dependent (TD)-DFT calculations on the same level of theory. Orbital plots were obtained using Jmol 14.27.2.
Partial charges were obtained with NBO 5.9[92] from the results of the DFT calculations.

5.2 Experiments to chapter 3.1.1 – 3.1.5

General procedure of Sonogashira-Hagihara coupling (Procedure 1)

The reactions were carried out under a nitrogen atmosphere. A mixture of 5 mmol of aryl halides, 1 mol % of $Pd(PPh_3)_2Cl_2$, and 2 mol % of CuI was suspended in 7 mL of dry NEt_3 with stirring. A sample of the corresponding ethyne (1.05 equiv) in dry NEt_3 was added dropwise at ambient temperature. The resulting solutions were then stirred at reflux temperature until complete conversion was monitored by TLC. The mixtures were then allowed to cool to rt. The solvents were removed *in vacuo*. The resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.

2-Methyl-4-(quinolin-3-yl)but-3-yn-2-ol (34)



According to **Procedure 1**, a solution of 4.160 g (20.00 mmol) of 3-bromoquinoline **33a**, 0.140 g (0.2 mmol) of $Pd(PPh_3)_2Cl_2$, 0.076 g (0.4 mmol) of CuI and 2.05 mL (21.0 mmol) of MEBYNOL in 60 mL of anhydrous NEt_3 was heated over a period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 2:1) gave 2-methyl-4-(quinolin-3-yl)but-3-yn-2-ol **34**.

Yield: 4.051 g (96%) of a light brown solid.

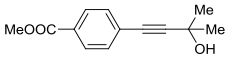
Mp: 113 °C.

^{1}H NMR (400 MHz, $CDCl_3$)[I]: δ = 8.95 (d, *J* = 2.0 Hz, 1H, 2-H), 8.29 (d, *J* = 2.0 Hz, 1H, 4-H), 8.10 (dd, *J* = 0.8, 8.4 Hz, 1H, 8-H), 7.78 (dd, *J* = 0.8, 8.4 Hz, 1H, 5-H), 7.74 (ddd, *J* = 1.5, 7.0, 8.4 Hz, 1H, 7-H), 7.55 (ddd, *J* = 1.5, 7.0, 8.4 Hz, 1H, 6-H), 4.46 (br s, 1H, O*H*), 1.68 (s, 6H, 2CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0 (+, C2), 146.4 (o, C8a), 138.8 (+, C4), 130.2 (+, C7), 129.0 (+, C8), 127.6 (+, C5), 127.4 (+, C6), 127.3 (o, C4a), 117.2 (o, C3), 98.2 (o, Cβ), 79.0 (o, Cα), 65.2 (+, *C*CH_3), 31.5 (+, *C*H_3) ppm.

IR (ATR): 3233, 2976, 2967, 2926, 1490, 1374, 1359, 1341, 1233, 1176, 1166, 1142, 963, 956, 911, 773, 751, 500, 463, 431 cm^{-1}.

Methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate (38)



According to **Procedure 1,** a solution of 4.300 g (20.00 mmol) of methyl 4-bromobenzoate **36**, 0.140 g (0.20 mmol) of $Pd(PPh_3)_2Cl_2$, 0.076 g (0.40 mmol) of CuI and 2.05 mL (21.00 mmol) of MEBYNOL in 60 mL of anhydrous NEt_3 was heated over a period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 2:1) gave methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate **38**.

Yield: 4.229 g (97%) of a yellow solid.

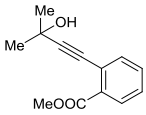
Mp: 85 °C.

[I] This spectrum is in agreement with previously reported spectral data[93]

^{1}H NMR (400 MHz, $CDCl_3$)[II]: δ = 7.97 (ddd, *J* = 1.5, 2.0, 8.2 Hz, 2H), 7.46 (ddd, *J* = 1.5, 2.0, 8.2 Hz, 2H), 3.91 (s, 3H), 2.29 (s, 1H), 1.63 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 131.6, 129.5, 129.4, 127.5, 96.8, 81.4, 65.6, 52.3, 31.4 ppm.

Methyl 2-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate



According to **Procedure 1,** a solution of 4.300 g (20.00 mmol) of methyl 2-bromobenzoate, 0.140 g (0.20 mmol) of $Pd(PPh_3)_2Cl_2$, 0.076 g (0.40 mmol) of CuI and 2.05 mL (21.00 mmol) of MEBYNOL in 60 mL of anhydrous NEt_3 was heated over a period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 2:1) gave methyl 2-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate.

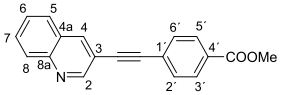
Yield: 3.837 g (88%) of a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$)[III]: δ = 7.97 (ddd, *J* = 1.5, 2.0, 8.2 Hz, 2H), 7.46 (ddd, *J* = 1.5, 2.0, 8.2 Hz, 2H), 3.92 (s, 3H), 1.64 (s, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.6, 133.9, 131.9, 131.6, 130.4, 127.9, 123.3, 96.8, 80.9, 65.6, 52.2, 31.4 ppm.

[II] This spectrum is in agreement with previously reported spectral data[93]
[III] This spectrum is in agreement with previously reported spectral data[94]

Methyl 4-(quinolin-3-ylethynyl)benzoate (37a)



According to **Procedure 1**, a solution of 2.150 g (10.00 mmol) of methyl 4-bromobenzoate **36**, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI and 2.184 g (10.50 mmol) of 3-ethynylquinoline **35** in 30 mL of anhydrous NEt_3 was heated for 1 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 4-(quinolin-3-ylethynyl)benzoate **37a**.

Yield: 2.153 g (75%) of a brown solid.

Mp: 138 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 2.2 Hz, 1H, 2-H), 8.33 (d, *J* = 2.2 Hz, 1H, 4-H), 8.11 (d, *J* = 8.6 Hz, 1H, 8-H), 8.06 (ddd, *J* = 1.4, 2.0, 8.3 Hz, 2H, 3′-H, 5′-H), 7.81 (d, *J* = 8.6 Hz, 1H, 5-H), 7.74 (ddd, *J* = 1.5, 6.8, 8.6 Hz, 1H, 7-H), 7.65 (ddd, *J* = 1.4, 2.0, 8.3 Hz, 2H, 2′-H, 4′-H), 7.58 (ddd, *J* = 1.5, 6.8, 8.6 Hz, 1H, 6-H), 3.94 (s, 3H, COOCH_3) ppm.

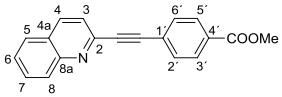
^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5 (o, *C*OO), 152.0 (+, C2), 147.0 (o, C8a), 138.7 (+, C4), 131.7 (+, C2′, C4′), 130.4 (+, C8), 130.0 (o, C4′), 129.7 (+, C3′, C5′), 129.5 (+, C7), 127.7 (+, C5), 127.5 (+, C6), 127.3 (o, C4a), 127.2 (o, C1′), 116.9 (o, C3), 91.8 (o, Cβ), 89.5 (o, Cα), 52.3 (+, *C*H_3) ppm.

IR (ATR): 3017, 1716, 1276, 1098, 953, 905, 855, 767, 742, 697, 480 cm^{-1}.

MS (ESI): *m/z* = 287.3 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1025, found 288.1022.

Methyl 4-(quinolin-2-ylethynyl)benzoate (37b)



According to **Procedure 1**, a solution of 0.327 g (2.00 mmol) of 2-cloroquinoline **33b**, 0.014 g (0.02 mmol) of $Pd(PPh_3)_2Cl_2$, 0.008 g (0.04 mmol) of CuI and 0.352 g (2.2 mmol) of methyl 4-ethynylbenzoate **39** in 7 mL of anhydrous NEt_3 was heated for 1 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 4-(quinolin-2-ylethynyl)benzoate **37b**.

Yield: 0.379 g (66%) of a brown solid.

Mp: 131 °C.

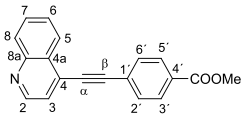
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.5 Hz, 1H, 4-H), 8.15 (d, *J* = 8.7 Hz, 1H, 8-H), 8.06–8.04 (m, 2H, 3′-H, 5′-H), 7.82 (dd, *J* = 1.2, 8.1 Hz, 1H, 5-H), 7.75 (ddd, *J* = 1.5, 6.9, 8.7 Hz, 1H, 7-H), 7.73–7.71 (m, 2H, 2′-H, 6′-H), 7.62 (d, *J* = 8.5 Hz, 1H, 3-H), 7.57 (ddd, *J* = 1.5, 6.9, 8.4 Hz, 1H, 6-H), 3.93 (s, 3H, COOC*H*$_3$) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.6 (o, COO), 148.2 (o, C8a), 143.1 (o, C2), 136.6 (+, C4), 132.3 (+, C2′, C6′), 130.6 (o, C4′), 130.5 (+, C7), 129.7 (+, C3′, C5′), 129.4 (+, C8), 127.7 (+, C5), 127.6 (+, C6), 127.4 (o, C4a), 126.8 (o, C1′), 124.4 (+, C3), 91.8 (o, Cβ), 89.2 (o, Cα), 52.4 (+, *C*H$_3$) ppm.

IR (ATR): 2946, 2847, 1943, 1712, 1591, 1496, 1436, 1306, 1275, 1175, 1106, 1012, 859, 829, 788, 767, 748, 697, 625, 504, 479 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1019, found 288.1028.

Methyl 4-(quinolin-4-ylethynyl)benzoate (37c)



According to **Procedure 1**, a solution of 0.416 g (2.00 mmol) of 4-bromoquinoline **33c**, 0.014 g (0.02 mmol) of $Pd(PPh_3)_2Cl_2$, 0.008 g (0.04 mmol) of CuI and 0.352 g (2.20 mmol) of methyl 4-ethynylbenzoate **39** in 7 mL of anhydrous NEt_3 was heated over a period of 1 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 4-(quinolin-4-ylethynyl)benzoate **37c**.

Yield: 0.448 g (78%) of a yellow solid.

Mp: 120 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 4.2 Hz, 1H, 2-H), 8.35 (d, *J* = 8.4 Hz, 1H, 5-H), 8.18 (d, *J* = 8.4 Hz, 1H, 8-H), 8.11–8.09 (m, 2H, 3′-H, 5′-H), 7.79 (ddd, *J* = 1.4, 6.9, 8.3, 1H, 6-H), 7.74–7.72 (m, 2H, 2′-H, 6′-H), 7.66 (ddd, *J* = 1.4, 6.9, 8.3, 1H, 7-H), 7.61 (d, *J* = 4.2 Hz, 1H, 3-H), 3.96 (s, 3H, COOCH_3) ppm.

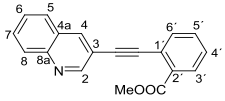
^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5 (o, *C*OO), 149.6 (+, C2), 147.9 (o, C8a), 132.1 (+, C2′, C6′), 130.7 (o, C4′), 130.4 (+, C7), 129.9 (+, C8), 129.6 (o, C4), 127.8 (o, C4a), 127.7 (+, C6), 126.9 (o, C1′), 126.0 (+, C5), 123.9 (+, C3), 97.1 (o, Cβ), 87.8 (o, Cα), 52.3 (+, *C*H_3) ppm.

IR (ATR): 3055, 2954, 2846, 1947, 1721, 1602, 1577, 1499, 1435, 1404, 1307, 1273, 1194, 1172, 1108, 1015, 959, 870, 854, 763, 691, 594, 525, 499, 458, 443 cm^{-1}.

MS (ESI): *m/z* = 288.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NNaO_2$ $[M+Na]^+$ 310.0833, found 310.0837.

Methyl 2-(quinolin-3-ylethynyl)benzoate (40)



According to **Procedure 1**, a solution of 2.150 g (10.00 mmol) of methyl 2-bromobenzoate, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI and 2.184 g (10.50 mmol) of 3-ethynylquinoline **35** in 30 mL of anhydrous NEt_3 was heated over a period of 1 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 2-(quinolin-3-ylethynyl)benzoate **40**.

Yield: 1.607 g (56%) of a light brownish solid.

Mp: 64 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.05 (d, *J* = 2.0 Hz, 1H, 2-H), 8.36 (d, *J* = 2.0 Hz, 1H, 4-H), 8.11 (d, *J* = 8.6 Hz, 1H, 8-H), 8.02 (dd, *J* = 1.5, 7.8 Hz, 1H, 6′-H), 7.81 (d, *J* = 8.6 Hz, 1H, 5-H), 7.76-7.69 (m, 2H, 3′-H, 7-H), 7.60–7.50 (m, 2H, 4′-H, 6-H), 7.42 (td, *J* = 1.3, 7.8 Hz, 1H, 5′-H), 3.99 (s, 3H, COOC*H*$_3$) ppm.

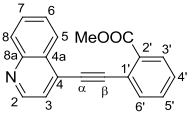
^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5 (o, *C*OO), 152.2 (+, C2), 147.0 (o, C8a), 138.5 (+, C4), 134.2 (+, C5′), 131.9 (o, C2′), 131.8 (+, C3′), 130.7 (+, C4′), 130.2(+, C8), 129.5 (+, C6′), 128.5 (+, C7), 127.7 (+, C5), 127.4 (+, C6), 127.3 (C4a), 123.1 (o, C1′), 117.5 (o, C3), 91.5 (o, Cβ), 91.4 (o, Cα), 52.3 (+, *C*H$_3$) ppm.

IR (ATR): 2952, 1731, 1565, 1485, 1435, 1270, 1250, 1111, 1076, 899, 746, 692, 471 cm^{-1}.

MS (ESI): *m/z* = 287.3 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1025, found 288.1030.

Methyl 2-(quinolin-4-ylethynyl)benzoate (41)



According to **Procedure 1**, a solution of 0.416 g (2.00 mmol) of 4-bromoquinoline **33c**, 0.014 g (0.02 mmol) of $Pd(PPh_3)_2Cl_2$, 0.008 g (0.04 mmol) of CuI and 0.352 g (2.20 mmol) of methyl 2-ethynylbenzoate in 7 mL of anhydrous NEt_3 was heated over a period of 1 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 2-(quinolin-4-ylethynyl)benzoate **41**.

Yield: 0.362 g (63%) of a yellow solid.

Mp: 57 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 4.4 Hz, 1H, 2-H), 8.54 (ddd, *J* = 0.5, 1.4, 8.3 Hz, 1H, 5-H), 8.14 (d, *J* = 8.3 Hz, 1H, 8-H), 8.06 (ddd, *J* = 0.5, 1.4, 7.9 Hz, 1H, 3′-H), 7.78 (ddd, *J* = 0.5, 1.3, 7.7 Hz, 1H, 6′-H), 7.77 (ddd, *J* = 1.5, 6.8, 8.4 Hz, 1H, 7-H), 7.66 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1H, 6-H), 7.61 (d, *J* = 4.4 Hz, 1H, 3-H), 7.57 (td, *J* = 1.4, 7.6 Hz, 1H, 5′-H), 7.48 (ddd, *J* = 1.3, 7.5, 7.9 Hz, 1H, 4′-H), 3.98 (s, 3H, CH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.4 (o, *C*OO), 149.7 (+, C2), 148.1 (o, C8a), 134.7 (+, C6′), 132.2 (o, C2′), 130.9 (+, C3′), 130.2 (+, C7), 130.1 (o, C4), 129.8 (+, C8), 129.1 (+, C4′), 128.0 (o, C4a), 127.5 (+, C6), 126.5 (+, C5), 123.9 (+, C3), 122.9 (o, C1′), 97.4 (o, Cβ), 90.0 (o, Cα), 52.5 (+, *C*H_3) ppm.

IR (ATR): 2953, 2215, 1950, 1921, 1709, 1595, 1576, 1502, 1427, 1391, 1295, 1127, 1070, 1042, 962, 880, 863, 839, 752, 695, 569, 547, 438 cm^{-1}.

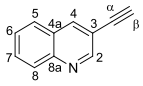
MS (ESI): *m/z* =288.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NNaO_2$ $[M+Na]^+$ 310.0833, found 310.0839.

General procedure of synthesis of terminal alkynes (Procedure 2)

The reactions were carried out under a nitrogen atmosphere. A flask was charged with the protected acetylenes (1.00 mmol), KOH (1.05 mmol), K_3PO_4 (1.05 mmol), and anhydrous toluene (40 mL). Then the flask was immersed into a preheated oil bath (200 °C). The suspensions were stirred vigorously under reflux temperature until complete conversion, as monitored by TLC. The mixtures were then allowed to cool to rt and filtered through a plug of celite, which was washed several times with toluene. After evaporation of the organic phase to dryness, the resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.

3-Ethynylquinoline (35)



According to **Procedure 2**, a solution of 3.165 g (15.00 mmol) of 2-methyl-4-(quinolin-3-yl)but-3-yn-2-ol, 0.882 g (15.75 mmol) of KOH and 3.339 g (15.75 mmol) of K_3PO_4 in 50 mL of anhydrous toluene was heated for 0.25 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-ethynylquinoline **35**.

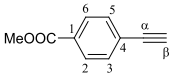
Yield: 2.180 g (95%) of colorless crystals.

Mp: 81 °C

^{1}H NMR (400 MHz, $CDCl_3$)[IV]: δ = 8.95 (d, *J* = 1.8 Hz, 1H, 2-H), 8.30 (d, *J* = 1.8 Hz, 1H, 4-H), 8.10 (dd, *J* = 0.8, 8.5 Hz, 1H, 8-H), 7.79 (dd, *J* = 0.8, 8.5 Hz, 1H, 5-H), 7.74 (ddd, *J* = 1.3, 6.9, 8.5 Hz, 1H, 7-H), 7.57 (ddd, *J* = 1.3, 6.9, 8.5 Hz, 1H, 6-H), 3.28 (s, 1H, C*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3 (+, C2), 147.1 (o, C8a), 139.4 (+, C4), 130.4 (+, C8), 129.5 (+, C7), 127.6 (+, C6), 127.4 (+, C5), 127.0 (o, C4a), 116.3 (o, C3), 81.0 (o, Cα), 80.5 (+, Cβ) ppm.

Methyl 4-ethynylbenzoate (39)



According to **Procedure 2**, a solution of 3.27 g (15.00 mmol) of methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate, 0.882 g (15.75 mmol) of KOH and 3.339 g (15.75 mmol) of K_3PO_4 in 50 mL of anhydrous toluene was heated over a period of 0.25 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 4-ethynylbenzoate **39**.

Yield: 2.376 g (99%) of colorless crystals.

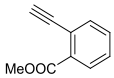
Mp: 93 °C.

[IV] This spectrum is in agreement with previously reported spectral data[93]

^{1}H NMR (400 MHz, $CDCl_3$)[V]: δ = 7.99 (ddd, *J* = 1.5, 1.8, 8.5 Hz, 2H), 7.55 (ddd, *J* = 1.5, 1.8, 8.5 Hz, 2H), 3.92 (s, 3H), 3.23 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 132.1, 130.1, 129.5, 126.8, 82.8, 80.1, 52.3 ppm.

Methyl 2-ethynylbenzoate



According to **Procedure 2**, a solution of 3.27 g (15.00 mmol) of methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate, 0.882 g (15.75 mmol) of KOH and 3.339 g (15.75 mmol) of K_3PO_4 in 50 mL of anhydrous toluene was heated over a period of 0.25 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave methyl 2-ethynylbenzoate.

Yield: 1.56 g (65%) of a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$)[VI]: δ = 7.94 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 3.40 (s, 1H) ppm.

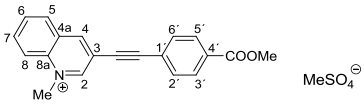
^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 138.0, 132.5, 131.7, 130.3, 128.5, 122.7, 82.3, 82.0, 52.2 ppm.

[V] This spectrum is in agreement with previously reported spectral data[94]
[VI] This spectrum is in agreement with previously reported spectral data[95]

General procedure for the preparation of the salts (Procedure 3)

Samples of 0.50 mmol of the corresponding esters were dissolved in toluene containing 1 drop of nitrobenzene. Then 0.75 mmol of dimethyl sulfate was added with stirring. Thereafter the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 × 10 mL), and dried to afford the product.

3-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (42a)



According to **Procedure 3**, a solution of 1.435 g (5.00 mmol) of methyl 4-(quinolin-3-ylethynyl)benzoate **37a**, 1 drop of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated for 1.5 h under reflux temperature to give 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **42a**.

Yield: 1.858 g (90%) of a brownish solid.

Mp: 219.8 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.91 (d, *J* = 1.2 Hz, 1H, 2-H), 9.54 (d, *J* = 1.2 Hz, 1H, 4-H), 8.55 (d, *J* = 9.0 Hz, 1H, 8-H), 8.46 (d, *J* = 9.0 Hz, 1H, 5-H), 8.33 (ddd, *J* =1.3, 7.0, 9.0 Hz, 1H, 6-H), 8.14–8.07 (m, 3H, 7-H, 2′-H, 6′-H), 7.83 (ddd, *J* = 1.5, 1.9, 8.2 Hz, 2H, 3′-H, 5′-H), 4.66 (s, 3H, NCH_3), 3.90 (s, 3H, COOCH_3), 3.37 (s, 3H, CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.5 (o, *C*OO), 152.2 (+, C2), 148.3 (+, C4), 137.5 (o, C8a), 136.3 (+, C7), 132.1 (+, C2′, C6′), 130.7 (+, C6), 130.5 (o, C4a), 130.4

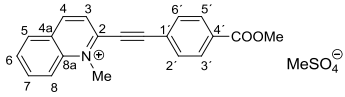
(+, C5), 129.7 (+, C3′, C5′), 128.7 (o, C4′), 125.2 (C1′), 119.3 (+, C8), 116.2 (o, C3), 93.5 (o, Cα), 85.9 (o, Cβ), 52.8 (+, CH_3SO_4), 52.5 (+, $COOCH_3$), 45.5 (+, NCH_3) ppm.

IR (ATR): 1721, 1278, 1240, 1215, 1170, 1097, 1057, 1005, 866, 766, 729, 696, 607, 574 cm^{-1}.

MS (ESI): *m/z* = 302.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ $[M]^+$ 302.1181, found 302.1183.

2-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (42b)



According to **Procedure 3**, a solution of 0.287 g (1.00 mmol) of methyl 4-(quinolin-2-ylethynyl)benzoate **37b**, 1 drop of nitrobenzene and 0.24 mL (2.50 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 2-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **42b**.

Yield: 0.404 g (98%) of a gray solid.

Mp: 185 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.27 (d, *J* = 8.3 Hz, 1H, 4-H), 8.62 (d, *J* = 9.0 Hz, 1H, 8-H), 8.48 (d, *J* = 8.3 Hz, 1H, 3-H), 8.46 (d, *J* = 6.2 Hz, 1H, 5-H), 8.32 (ddd, *J* = 1.6, 7.2, 8.8 Hz, 1H, 7-H), 8.15 (d, *J* = 8.3 Hz, 2H, 3′-H, 5′-H), 8.10 (d, *J* = 8.3 Hz, 2H, 2′-H, 6′-H) 8.07 (t, *J* = 7.6 Hz, 1H, 6-H), 4.79 (s, 3H, NCH_3), 3.91 (s, 3H, $COOCH_3$), 3.37 (s, 3H, CH_3SO_4) ppm.

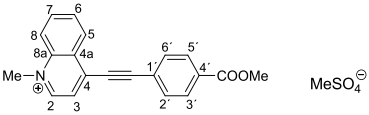
^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.3 (o, *C*OO), 145.6 (+, C4), 140.3 (o, C2), 139.4 (o, C8a), 136.2 (+, C7), 133.4 (+, C2′, C6′), 132.2 (o,C4′), 130.3 (+, C5), 129.7 (+, C6, C3′, C5′), 128.6 (o, C4a), 126.3 (+, C3), 123.3 (o, C1′), 119.6 (+, C8), 106.5 (o, Cα), 84.3 (o, Cβ), 52.7 (+, *C*H_3SO_4), 52.6 (+, COO*C*H_3), 42.9 (+, N*C*H_3) ppm.

IR (ATR): 3090, 3066, 2950, 2206, 2066, 1976, 1714, 1594, 1576, 1520, 1435, 1354, 1221, 1106, 1058, 1004, 831, 770, 732, 694, 609, 577, 498, 465, 428 cm^{-1}.

MS (ESI): *m/z* = 302.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ $[M]^+$ 302.1170, found 302.1170.

4-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (42c)



According to **Procedure 3**, a solution of 0.287 g (1.00 mmol) of methyl 4-(quinolin-4-ylethynyl)benzoate **37c**, 1 drop of nitrobenzene and 0.24 mL (2.50 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 4-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **42c**.

Yield: 0.401 g (97%) of a yellow solid.

Mp: 199 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.52 (d, *J* = 6.2 Hz, 1H, 2-H), 8.78 (d, *J* = 8.2 Hz, 1H, 5-H), 8.57 (d, *J* = 8.2 Hz, 1H, 8-H), 8.41 (d, *J* = 6.2 Hz, 1H, 3-H), 8.35 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7-H), 8.16 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 6-H), 8.13–8.11 (m, 2H, 3′-H,

5′-H), 8.06–8.05 (m, 2H, 2′-H, 6′-H), 4.64 (s, 3H, NC*H*$_3$) 3.91 (s, 3H, COOC*H*$_3$), 3.37 (s, 3H, C*H*$_3$SO$_4$) ppm.

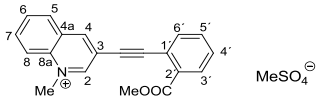
^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.4 (o, *C*OO), 149.5 (+, C2), 138.4 (o, C8a), 137.9 (o, C4), 135.8 (+, C7), 133.1 (+, C2′, C6′), 130.9 (+, C6), 129.6 (+, C3′, C5′), 128.4 (o, C4a), 127.9 (+, C5), 124.6 (+, C3), 124.4 (o, C1′), 119.8 (+, C8), 105.2 (o, Cα), 86.0 (o, Cβ), 52.8 (+, *C*H$_3$SO$_4$), 52.6 (+, COO*C*H$_3$), 45.5 (+, N*C*H$_3$) ppm.

IR (ATR): 3081, 2943, 2829, 2209, 1943, 1718, 1604, 1527, 1435, 1403, 1275, 1220, 1103, 1059, 1011, 863, 808, 784, 768, 727, 694, 645, 608, 577, 551, 466, 428 cm^{-1}.

MS (ESI): *m/z* = 302.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ [M]$^+$ 302.1170, found 302.1192.

3-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (43)



According to **Procedure 3,** a solution of 1.435 g (5.00 mmol) of methyl 2-(quinolin-3-ylethynyl)benzoate **40**, 1 drop of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated for 1.5 h under reflux temperature to give 3-((2-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **43**.

Yield: 1.920 g (93%) of a yellow solid.

Mp: 217 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.80 (d, *J* = 1.0 Hz, 1H, 2-H), 9.47 (d, *J* = 1.0 Hz, 1H, 4-H), 8.54 (d, *J* = 9.1 Hz, 1H, 8-H), 8.50 (d, *J* = 9.1 Hz, 1H, 5-H), 8.32 (ddd, *J* = 1.5, 7.1, 9.1 Hz, 1H, 6-H), 8.11 (ddd, *J* = 1.5, 7.1, 9.1 Hz, 1H, 7-H), 8.04 (dd, *J* = 1.0, 8.0 Hz, 1H, 6′-H), 7.85 (dd, *J* = 1.0, 8.0 Hz, 1H, 3′-H), 7.76 (td, *J* = 1.5, 7.6 Hz, 1H, 4′-H), 7.66 (td, *J* = 1.5, 7.6 Hz, 1H, 5′-H), 4.66 (s, 3H, NCH_3), 3.96 (s, 3H, COOCH_3), 3.36 (s, CH_3SO$_4$) ppm.

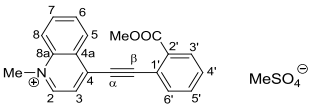
^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.5 (o, *C*OO), 151.9 (+, C2), 148.0 (+, C4), 137.4 (o, C8a), 136.1 (+, C7), 134.3 (+, C5′), 132.7 (+, C6′), 131.8 (o, C2′), 130.6 (+, C6), 130.5 (+, C4′), 130.4 (+, C5), 130.2 (+, C3′), 128.8 (o, C4a), 120.7 (o, C1′), 119.2 (+, C8), 116.8 (o, C3), 93.4 (o, Cα), 87.4 (o, Cβ), 52.8 (+, *C*H$_3$SO$_4$), 52.5 (+, COO*C*H$_3$), 45.5 (+, NCH$_3$) ppm.

IR (ATR): 2923, 2219, 1737, 1272, 1258, 1133, 1082, 832, 765, 761, 698, 556, 434 cm^{-1}.

MS (ESI): *m/z* = 302.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ [M]$^+$ 302.1188, found 302.1181.

4-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (44)



According to **Procedure 3**, a solution of 0.144 g (0.50 mmol) of methyl 2-(quinolin-4-ylethynyl)benzoate **41**, 1 drop of nitrobenzene and 0.711 mL (0.75 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 1.5 h under reflux temperature to give 4-((2-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **44**.

Yield: 0.196 g (95%) of a light green solid.

Mp: 109 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.50 (d, *J* = 5.8 Hz, 1H, 2-H), 8.85 (d, *J* = 8.3 Hz, 1H, 5-H), 8.56 (d, *J* = 8.6 Hz, 1H, 8-H), 8.35-8.32 (m, 2H, 3-H, 7-H), 8.16 (t, *J* = 7.6 Hz, 1H, 6-H), 8.09 (d, *J* = 7.7 Hz, 1H, 3′-H), 8.04 (d, *J* = 7.5 Hz, 1H, 6′-H), 7.82 (t, *J* = 7.3 Hz, 1H, 5′-H), 7.75 (t, *J* = 7.6 Hz, 1H, 4′-H), 4.64 (s, 3H, NCH_3) 3.97 (s, 3H, COOCH_3), 3.38 (s, 3H, CH_3SO$_4$) ppm.

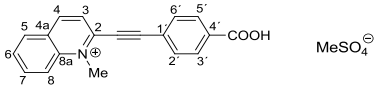
^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.3 (o, *C*OO), 149.5 (+, C2), 138.5 (o, C4), 138.4 (o, C8a), 135.7 (+, C7), 135.4 (+, C6′), 132.9 (+, C5′), 132.0 (o, C2′), 131.4 (+, C4′), 130.7 (+, C6), 128.6 (o, C4a), 127.9 (+, C5), 124.5 (+, C3), 120.0 (o, C1′), 119.8 (+, C8), 105.4 (o, Cβ), 87.9 (o, Cα), 52.8 (+, *C*H$_3$SO$_4$), 52.7 (+, COO*C*H$_3$), 45.4 (+, N*C*H$_3$) ppm.

IR (ATR): 3076, 3025, 2949, 2202, 1726, 1603, 1572, 1527, 1494, 1486, 1436, 1401, 1228, 1164, 1079, 1059, 1010, 845, 760, 726, 694, 608, 576, 550, 429 cm^{-1}.

MS (ESI): *m/z* = 302.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ [M]$^+$ 302.1181, found 302.1187.

2-((4-Carboxyphenyl)ethynyl)-1-methylquinolinium methylsulfate (60b)



According to **Procedure 3**, a suspension of 0.273 g (1.00 mmol) of 4-(quinolin-2-ylethynyl)benzoic acid **66b**, 1 drop of nitrobenzene and 0.24 mL (2.50 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux

temperature to give 2-((4-carboxyphenyl)ethynyl)-1-methylquinolinium methylsulfate **60b**.

Yield: 0.331 g (83%) of a yellow solid.

Mp: 177 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.26 (d, *J* = 8.7 Hz, 1H, 4-H), 8.61 (d, *J* = 8.9 Hz, 1H, 8-H), 8.50 (d, *J* = 8.3 Hz, 1H, 5-H), 8.47 (d, *J* = 8.7 Hz, 1H, 3-H), 8.32 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 8.13 (d, *J* = 8.7 Hz, 2H, 3′-H, 5′-H), 8.07 (d, *J* = 8.5 Hz, 2H, 2′-H, 6′-H) 8.07 (t, *J* = 7.6 Hz, 1H, 6-H), 4.79 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

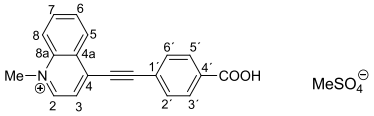
^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.3 (o, *C*OO), 145.6 (+, C4), 140.4 (o, C2), 139.4 (o, C8a), 136.2 (+, C7), 133.5 (o,C4′), 133.3 (+, C2′, C6′), 130.4 (+, C5), 129.7 (+, C6), 129.6 (+, C3′, C5′), 128.6 (o, C4a), 126.3 (+, C3), 122.8 (o, C1′), 119.6 (+, C8), 106.8 (o, Cα), 84.1 (o, Cβ), 52.7 (+, *C*H_3SO_4), 42.9 (+, N*C*H_3) ppm.

IR (ATR): 2944, 2220, 1717, 1635, 1609, 1521, 1489, 1407, 1387, 1334, 1171, 1057, 994, 866, 842, 746, 689, 659, 612, 575, 471, 427 cm^{-1}.

MS (ESI): *m/z* = 288.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M]^+$ 288.1014, found 288.1031.

4-((4-Carboxyphenyl)ethynyl)-1-methylquinolinium methylsulfate (60c)



According to **Procedure 3**, a suspension of 0.273 g (1.00 mmol) of 4-(quinolin-4-ylethynyl)benzoic acid **66c**, 1 drop of nitrobenzene and 0.24 mL (2.50 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 4-((4-carboxyphenyl)ethynyl)-1-methylquinolinium methylsulfate **60c**.

Yield: 0.343 g (86%) of a yellow solid.

Mp: 195 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.51 (d, *J* = 5.8 Hz, 1H, 2-H), 8.78 (d, *J* = 8.1 Hz, 1H, 5-H), 8.56 (d, *J* = 8.8 Hz, 1H, 8-H), 8.40 (d, *J* = 5.8 Hz, 1H, 3-H), 8.35 (t, *J* = 7.7 Hz, 1H, 7-H), 8.16 (t, *J* = 7.7 Hz, 1H, 6-H), 8.10 (d, *J* = 7.9 Hz, 2H, 3′-H, 5′-H), 8.03 (d, *J* = 8.3 Hz, 2H, 2′-H, 6′-H), 4.63 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.5 (o, COO), 149.5 (+, C2), 138.4 (o, C8a), 138.0 (o, C4), 135.8 (+, C7), 132.9 (o, C4′), 131.0 (+, C6), 129.8 (+,C3′, C5′), 128.5 (o, C4a), 128.0 (+, C5), 124.6 (o, C1′), 124.0 (+, C3), 119.9 (+, C8), 105.6 (o, Cβ), 85.8 (o, Cα), 52.8 (+, *C*H$_3$SO$_4$), 45.5 (+, NCH$_3$) ppm.

IR (ATR): 2207, 1706, 1615, 1604, 1572, 1531, 1403, 1370, 1256, 1195, 1108, 1054, 997, 872, 837, 751, 676, 610, 578, 484, 432 cm^{-1}.

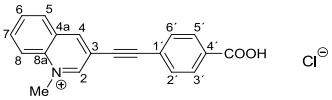
MS (ESI): *m/z* = 288.0 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ [M]$^+$ 288.1014, found 288.1023.

General procedure for the ester hydrolysis (Procedure 4)

The corresponding salt (1.00 mmol) was dissolved in methanol (5 mL) and then sodium hydroxide (1N in water, 10 equiv) was added with stirring. The resulting mixture was stirred overnight. Then, the solution was acidified using concentrated HCl and then concentrated *in vacuo*; the crude product was purified by column chromatography with methanol-chloroform as eluent.

3-((4-Carboxyphenyl)ethynyl)-1-methylquinolinium chloride (60a)



According to **Procedure 4**, a solution of 0.826 g (2.00 mmol) of 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **42a** and 0.800 g (20.00 mmol) of NaOH in 25 mL of the methanol-water mixture was stirred over the perion of 12 h under rt. Then, the solution was acidified (pH = 1) and then concentrated *in vacuo*. Finally, a purification by column chromatography (methanol: chloroform = 1:3) gave 3-((4-carboxyphenyl)ethynyl)-1-methylquinolinium chloride **60a**.

Yield: 0.594 g (92%) of a brownish solid.

Mp: 97 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.97 (d, *J* = 1.2 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 8.55 (d, *J* = 9.0 Hz, 1H, 8-H), 8.47 (d, *J* = 9.0 Hz, 1H, 5-H), 8.32 (ddd, *J* = 1.3, 6.9, 9.0 Hz, 1H, 7-H), 8.10 (t, *J* = 9.0 Hz, 1H, 6-H), 8.06 (ddd, *J* = 1.5, 1.9, 8.3 Hz, 2H, 3′-H, 5′-H), 7.79 (ddd, *J* = 1.5, 1.9, 8.3 Hz, 2H, 2′-H, 6′-H), 4.67 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.5 (o, *C*OO), 152.2 (+, C2), 148.2 (+, C4), 137.4 (o, C9), 136.2 (+, C7), 131.9 (+, C2′, C6′), 131.8 (o, C4′), 130.6 (+, C6), 130.4 (+,

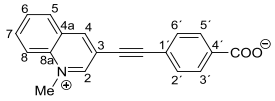
C5), 129.8 (+, C3′, C5′), 128.7 (o, C4a), 124.7 (o, C1′), 119.2 (+, C8), 116.3 (o, C3), 93.7 (o, Cα), 85.6 (o, Cβ), 45.4 (+, N*C*H$_3$) ppm.

IR (ATR): 3031, 2211, 1695, 1596, 1543, 1520, 1353, 1273, 1253, 1158, 1012, 770, 748, 694, 626, 478, 434 cm^{-1}.

MS (ESI): *m/z* = 288.0 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ [M]$^+$ 288.1025, found 288.1022.

4-((1-Methylquinolinium-3-yl)ethynyl)benzoate (61a)



To a solution of 0.080 g (0.25 mmol) of 3-((4-carboxyphenyl)ethynyl)-1-methylquinolinium chloride **60a** in methanol (4 mL) was added 0.042 mL (0.30 mmol) of NEt$_3$. The resulting mixture was stirred for 0.25 h at rt and then dried *in vacuo*. The residue was chromatographed on silica gel (methanol-chloroform).

Yield: 0.064 g (90%) of a light green solid.

Mp: 196 °C.

^{1}H NMR (400 MHz, CD_3OD): δ = 9.67 (s, 1H, 2-H), 9.32 (s, 1H, 4-H), 8.51 (d, *J* = 8.8 Hz, 1H, 8-H), 8.41 (d, *J* = 8.8 Hz, 1H, 5-H), 8.30 (ddd, *J* = 1.3, 7.0, 8.8 Hz, 1H, 7-H), 8.09 (t, *J* = 8.8 Hz, 1H, 6-H), 7.98 (d, *J* = 8.6 Hz, 2H, 3′-H, 5′-H), 7.61 (d, *J* = 8.6 Hz, 2H, 2′-H, 6′-H), 4.73 (s, 3H, NC*H$_3$*) ppm.

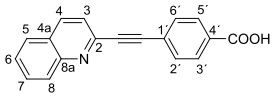
^{13}C NMR (100 MHz, CD_3OD): δ = 169.5 (o, *C*OO), 153.2 (+, C2), 149.5 (o, C4), 140.3 (o, C9), 139.1 (o, C4′), 137.5 (+, C7), 132.5 (+, C2′, C6′), 132.0 (+, C7), 131.7 (+, C5), 130.8 (o, C4a), 130.6 (+, C3′, C5′), 124.0 (o, C1′), 119.9 (+, C8), 119.5 (o, C3), 96.7 (o, Cα), 84.6 (o, Cβ), 46.4 (+, N*C*H$_3$) ppm.

IR (ATR): 2183, 1584, 1541, 1415, 1385, 1283, 848, 779, 745, 695 cm^{-1}.

MS (ESI): *m/z* = 288.0 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1025, found 288.1022.

4-(Quinolin-2-ylethynyl)benzoic acid (66b)



Methyl 4-(quinolin-2-ylethynyl)benzoate **37b** (0.287 g, 1.00 mmol) was dissolved in methanol (6 mL) and then NaOH (0.400 g, 10.00 mmol) in water (3 mL) was added with stirring. The resulted mixture was stirred overnight. The solution was acidified (pH = 1) and then concentrated *in vacuo* and the crude product was filtered off, washed with methanol (10 mL) and water (3 × 5 mL) to give **66b**.

Yield: 0.265 g (97%) of a yellow solid.

Mp: 181 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.50 (d, *J* = 8.3 Hz, 1H, 4-H), 8.05 (d, *J* = 7.8 Hz, 1H, 5-H), 8.05 (d, *J* = 8.2 Hz, 1H, 8-H), 8.03 (d, *J* = 8.5 Hz, 2H, 3′-H, 5′-H) 7.85 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, 7-H), 7.82–7.80 (m, 3H, 3-H, 2′-H, 6′-H), 7.69 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H, 6-H) ppm.

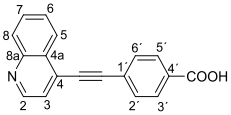
^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.6 (o, *C*OO), 147.3 (o, C8a), 142.0 (o, C2), 137.2 (+, C4), 132.1 (+, C2′, C6′), 131.5 (o, C4′), 130.7 (+, C7), 129.7 (+, C3′, C5′), 128.3 (+, C8), 128.1 (+, C5), 127.7 (+, C6), 127.1 (o, C4a), 125.4 (o, C1′), 124.4 (+, C3) 91.4 (o, Cβ), 88.6 (o, Cα) ppm.

IR (ATR): 2209, 1932, 1715, 1625, 1602, 1590, 1501, 1484, 1405, 1384, 1332, 1205, 1176, 1153, 1117, 1018, 963, 906, 874, 856, 843, 827, 765, 755, 685, 659, 621, 556, 522, 468 cm^{-1}.

MS (ESI): *m/z* = 274.0 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{18}H_{12}NO_2$ $[M+H]^+$ 274.0863, found 274.0855.

4-(Quinolin-4-ylethynyl)benzoic acid (66c)



Methyl 4-(quinolin-4-ylethynyl)benzoate **37c** (0.287 g, 1.00 mmol) was dissolved in methanol (6 mL) and then NaOH (0.400 g, 10.00 mmol) in water (3 mL) was added with stirring. The resulted mixture was stirred overnight. The solution was acidified (pH = 1) and then concentrated *in vacuo* and the crude product was filtered off, washed with methanol (10 mL) and water (3 × 5 mL) to give **66c**.

Yield: 0.240 g (88%) of a gray solid.

Mp: 274 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 13.27 (br s, 1H, COO*H*), 8.97 (d, *J* = 4.4 Hz, 1H, 2-H), 8.39 (dd, *J* = 1.2, 8.3 Hz, 1H, 5-H), 8.11 (d, *J* = 8.3 Hz, 1H, 8-H), 8.05–8.04 (m, 2H, 3′-H, 5′-H), 7.90–7.88 (m, 2H, 2′-H, 6′-H), 7.87 (ddd, *J* = 1.5, 6.9, 8.2 Hz, 1H, 7-H), 7.80 (d, *J* = 4.4 Hz, 1H, 3-H), 7.78 (ddd, *J* = 1.2, 6.9, 8.3 Hz, 1H, 6-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.6 (o, *C*OO), 150.2 (+, C2), 147.5 (o, C8a), 132.1 (+, C2′, C6′), 131.5 (o, C4′), 130.4 (+, C7), 129.7 (+,C8, C3′, C5′), 127.7 (+, C6), 126.6 (o, C4a), 125.6 (+, C5), 125.5 (o, C1′), 124.1 (+, C3), 97.4 (o, Cα), 87.1 (o, Cβ) ppm.

IR (ATR): 2207, 1703, 1606, 1583, 1499, 1417, 1403, 1391, 1307, 1272, 1167, 1016, 893, 858, 813, 757, 685, 608, 573, 537, 505, 471, 438 cm^{-1}.

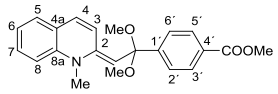
MS (ESI): *m/z* = 274.0 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{18}H_{12}NO_2$ $[M+H]^+$ 274.0863, found 274.0867.

The reaction of 42b with NaOH (Synthesis 62, 63)

2-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (**42b**; 0.413 g, 1.00 mmol, 100 mol %) was dissolved in methanol (6 mL) and then NaOH (0.400 g, 10.00 mmol, 1000 mol %) in water (3 mL) was added with stirring. The resulted mixture was stirred overnight. Then precipitated solid was filtered off and washed with methanol and water to give **62**. The solution was acidified (pH = 1) and then concentrated *in vacuo*, and the crude product was purified by column chromatography with $CHCl_3$-MeOH as eluent to give **63**.

Methyl 4-(1,1-dimethoxy-2-(1-methylquinolin-2(1H)-ylidene)ethyl)benzoate (62)



Yield: 0.095 g (26%) of a deep green solid.

Mp: 131 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.6 Hz, 2H, 3′-H, 5′-H), 7.70 (d, *J* = 8.8 Hz, 2H, 2′-H, 6′-H), 7.18 (ddd, *J* = 1.5, 7.3, 8.6 Hz, 1H, 7-H), 7.01 (dd, *J* = 1.5, 7.3 Hz, 1H, 5-H), 6.83 (d, *J* = 8.3 Hz, 1H, 8-H), 6.77 (td, *J* = 0.9, 7.4 Hz, 1H, 6-H), 6.68 (d, *J* = 9.8 Hz, 1H, 3-H), 6.49 (d, *J* = 9.8 Hz, 1H, 4-H), 4.46 (s, 1H, vinylic H), 3.89 (s, 3H, COOC*H*$_3$), 3.20 (s, 3H, NC*H*$_3$), 3.13 (s, 6H, OC*H*$_3$) ppm.

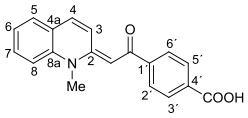
^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.2 (o, *C*OO), 148.6 (o, C1′), 142.4 (o, C8a), 141.9 (o, C2), 129.6 (+, C7), 129.2 (+,C3′, C5′), 129.1 (o, C4′), 127.5 (+, C5), 127.47 (+, C4), 127.3 (+,C2′, C6′), 122.0 (o, C4a), 120.7 (+, C3), 119.3 (+, C6), 111.9 (+, C8), 103.1 (o, CH_3OCOCH_3), 97.1 (+, vinylic C), 52.1 (+, COO*C*H$_3$), 48.6 (+, O*C*H$_3$), 34.0 (+, N*C*H$_3$) ppm.

IR (ATR): 2996, 2936, 2899, 2826, 1722, 1638, 1576, 1434, 1273, 1143, 1104, 1063, 1050, 1018, 959, 902, 859, 807, 732, 714, 564, 459 cm^{-1}.

MS (ESI): *m/z* = 366.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{22}H_{23}NO_4$ $[M+H]^+$ 366.1700, found 366.1710.

1-(4-Carboxyphenyl)-2-(1-methylquinolinium-2-yl)ethenolate (63)



Yield: 0.214 g (70%) of an orange solid.

Mp: 202 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.06 (d, *J* = 9.6 Hz, 1H, 4-H), 8.00 (d, *J* = 8.3 Hz, 2H, 3′-H, 5′-H), 7.96 (d, *J* = 8.5 Hz, 2H, 2′-H, 6′-H), 7.73 (d, *J* = 5.3 Hz, 1H, 3-H), 7.72 (d, *J* = 4.3 Hz, 1H, 8-H), 7.66 (dd, *J* = 1.6, 7.8 Hz, 1H, 5-H), 7.61 (ddd, *J* = 1.5, 7.2, 8.7 Hz, 1H, 7-H), 7.28 (m, 1H, 6-H), 6.10 (s, 1H, vinylic H), 3.74 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 184.6 (o, *C*O), 153.1 (o, C2), 144.6 (o, C1′), 139.8 (o, C8a), 137.6 (o, C4′), 134.3 (+, C3), 131.2 (+, C7), 129.0 (+,C3′, C5′), 128.3 (+, C5), 126.6 (+,C2′, C6′), 123.0 (o, C4a), 122.7 (+, C6), 121.2 (+, C4), 115.5 (+, C8), 90.1 (+, vinylic C), 35.2 (+, N*C*H_3) ppm.

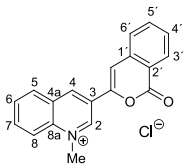
IR (ATR): 3449, 3284, 1632, 1607, 1593, 1548, 1508, 1487, 1433, 1392, 1358, 1344, 1208, 1110, 1060, 995, 900, 828, 736, 566, 433 cm^{-1}.

MS (ESI): *m/z* = 306.0 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{15}NNaO_3$ $[M+Na]^+$ 328.0939, found 328.0931.

1-Methyl-3-(1-oxo-1H-isochromen-3-yl)quinolinium chloride (61)

3-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (**42a**) (0.256 g, 0.60 mmol) was dissolved in methanol (50 mL) and then sodium hydroxide (10 equiv) was added with stirring. The resulting mixture was stirred over a period of 24 h. Then, the solution was acidified (pH = 1) followed by neutralization with sodium bicarbonate, and concentrated *in vacuo*. The crude product was purified by column chromatography with methanol-chloroform as an eluent.



Yield: 0.140 g (70%) of a yellow solid.

Mp: >275 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 9.99 (d, *J* = 1.3 Hz, 1H, 2-H), 9.67 (s, 1H, 4-H), 8.56–8.52 (m, 2H, 5-H, 8-H), 8.35–8.30 (m, 2H, 7-H, 8′-H), 8.13-8.08 (m, 1H, 6-H), 7.95–7.90 (m, 1H, 6′-H), 7.81–7.79 (m, 2H, 4′-H, 5′-H), 7.73–7.68 (m, 1H, 7′-H), 4.56 (s, 3H, NC*H*$_3$) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 162.5 (o, C1′), 149.7 (o, C8a′), 148.8 (+, C2), 148.59 (o, C3′) 143.1 (+, C4), 139,9 (o, C8a), 137.8 (+, C7), 137.0 (o, C6′), 135.6 (o), 133.6 (o), 132.2 (+, C6), 131.3 (+, C7′), 130.68 (+, C8′), 128.5 (+, C4′), 120.1 (+, C8), 107.4 (+, C4′), 46.7 (+, N*C*H$_3$) ppm.

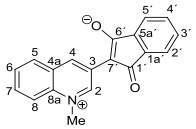
IR (ATR): 3098, 2836, 1638, 1587, 1565, 1486, 1455, 1363, 1345, 1330, 1320, 1250, 1210, 1172, 1124, 1109, 1074, 1044, 983, 921, 897, 807, 790, 778, 752, 726, 684, 665, 631, 553 cm^{-1}.

MS (ESI): *m/z* = 288.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M]^+$ 288.1025, found 288.1022.

2-(1-Methylquinolinium-3-yl)-1,3-dioxo-2,3-dihydro-1H-inden-2-ide (50)

3-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate (0.413 g; 1.00 mmol) was dissolved in methanol (5 mL) and then sodium hydroxide (1N in water, 10 equiv) was added with stirring. The resulting mixture was stirred overnight. Then, the solution was acidified (pH = 3) and then concentrated *in vacuo*, the crude product was purified by column chromatography with methanol-chloroform as an eluent.



Yield: 0.249 g (87%) of a red solid.

Mp: >300 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.44 (d, *J* = 1.5 Hz, 1H, 2-H), 9.74 (s, 1H, 4-H), 8.25 (d, *J* = 8.8 Hz, 1H, 8-H), 8.18 (m, 1H, 5-H), 7.85 (ddd, *J* = 1.5, 7.0, 8.8 Hz, 1H, 7-H), 7.78 (ddd, *J* = 0.9, 7.0, 8.0 Hz, 1H, 6-H), 7.42–7.40 (m, 2H, 3′-H, 4′-H), 7.35–7.34 (m, 2H, 2′-H, 5′-H), 4.56 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 189.4 (o, C1′, C6′), 145.7 (+, C2), 139.8 (o, C1a′, C5a′), 133.7 (o, C8a), 133.0 (o, C3), 131.3 (+, C4), 130.8 (+, C3′, C4′), 130.7 (+, C7), 130.1 (o, C4a), 129.1 (+, C6), 129.0 (+, C5), 118.6 (+, C8), 118.4 (+, C2′, C5′), 97.2 (o, C7′), 45.8 (+, NCH_3) ppm.

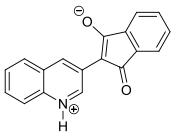
IR (ATR): 1599, 1227, 1203, 1160, 1436, 1407, 1373, 1348, 1338, 890, 758, 719, 510 cm^{-1}.

MS (ESI): *m/z* = 288.0 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M+H]^+$ 288.1025, found 288.1024.

1,3-Dioxo-2-(quinolinium-3-yl)-2,3-dihydro-1H-inden-2-ide (58) / sodium 1,3-dioxo-2-(quinolin-3-yl)-2,3-dihydro-1H-inden-2-ide (59)

Methyl 2-(quinolin-3-ylethynyl)benzoate (0.19 mmol) was dissolved in methanol (7 mL) and then potassium hydroxide (1N in water, 10 equiv) was added with stirring. The resulting mixture was stirred for 48 h. Then, the solution was acidified (pH = 1) and compound **58** precipitated. Then the product was filtered off and subsequently washed with water and with ethyl acetate, and finally dried *in vacuo*.



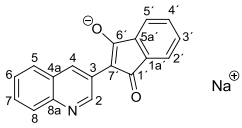
Yield: 0.363 g (70%) of an orange solid.

Mp: 122°C.

IR (ATR): 3060, 2440, 2051, 1977, 1929, 1677, 1609, 1559, 1432, 1355, 907, 867, 758, 717, 612, 548, 516, 468, 415 cm^{-1}.

MS (ESI): *m/z* = 272.0 $[M-H]^-$.

To obtain a soluble species for NMR experiment, the salt was neutralized with NaOH in water – methanol mixture and dried *in vacuo*.



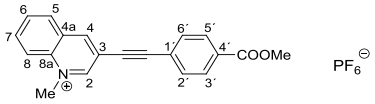
^{1}H NMR (600 MHz, CD_3OD): δ = 9.89 (s, 1H, 2-H), 9.04 (s, 1H, 4-H), 7.89 (d, 1H, *J* = 8.1 Hz, 8-H), 7.81 (d, 1H, *J* = 8.1 Hz, 5-H), 7.55-7.52 (m, 1H, 7-H), 7.48-7.46 (m, 1H, 6-H), 7.36-7.32 (m, 4H, 4′-H, 5′-H, 6′-H,7′-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 193.9 (o, C1′, C6′), 150.9 (+, C2), 144.9 (o, C8a), 141.1 (o, C1a′, C5a′), 132.1 (o, C3), 131.7 (+, C3′, C4′), 130.5 (o, C4a), 130.2 (+, C4), 128.7 (+, C5), 128.3 (+, C8), 128.2 (+, C7), 127.3 (+, C6), 119.2 (+, C2′, C5′), 103.3 (o, C7′) ppm.

General procedure of anion replacement to hexafluorophosphate (Procedure 5)

Corresponding salt was dissolved in water, then NH_4PF_6 (1.05 equiv) in water was added to the prepared solution. Hexafluorophosphate salt precipitated immediately. After 0.5 h the crude product was filtered off and washed with water (3 × 30 mL) and ethyl acetate (3 × 30 mL), dried *in vacuo* to give the desired product.

3-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate (42aPF$_6$)



According to **Procedure 5**, a solution of 0.036 g (0.088 mmol) of 3-((4 (methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate and 0.015 g (0.09 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) under rt to give 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate **42aPF$_6$**.

Yield: 0.037 g (95%) of an ivory solid.

Mp: 203 °C.

^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ = 9.91 (d, *J* = 1.2 Hz, 1H, 2-H), 9.54 (s, 1H, 4-H), 8.55 (d, *J* = 9.0 Hz, 1H, 8-H), 8.46 (d, *J* = 9.0 Hz, 1H, 5-H), 8.33 (ddd, *J* =1.3, 7.0, 9.0 Hz, 1H, 6-H), 8.14–8.07 (m, 3H, 7-H, 2′-H, 6′-H), 7.83 (ddd, *J* = 1.5, 1.9, 8.2 Hz, 2H, 3′-H, 5′-H), 4.66 (s, 3H, NC*H*$_3$), 3.90 (s, 3H, COOC*H*$_3$) ppm.

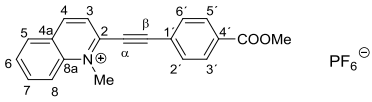
^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ = 165.4 (o, *C*OO), 152.2 (+, C2), 148.3 (+, C4), 137.5 (o, C8a), 136.3 (+, C7), 132.1 (+, C2′, C6′), 130.7 (+, C6), 130.5 (o, C4a), 130.4 (+, C5), 129.7 (+, C3′, C5′), 128.7 (o, C4′), 125.2 (C1′), 119.3 (+, C8), 116.2 (o, C3), 93.5 (o, Cβ), 85.9 (o, Cα), 52.5 (+, COO*C*H$_3$), 45.5 (+, N*C*H$_3$) ppm.

IR (ATR): 3097, 2228, 1724, 1519, 1436, 1376, 1312, 1276, 1188, 1182, 1172, 1098, 1018, 974, 964, 924, 835, 766, 697, 644, 623, 557 cm^{-1}.

MS (ESI): *m/z* = 302.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ [M]$^+$ 302.1181, found 302.1183.

2-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate (42bPF$_6$)



According to **Procedure 5**, a solution of 0.036 g (0.088 mmol) of 2-((4 (methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate and 0.015 g (0.09 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred for 0.5 h under rt to give 2-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate **42bPF$_6$**.

Yield: 0.038 g (97%) of a white purple solid.

Mp: 224 °C.

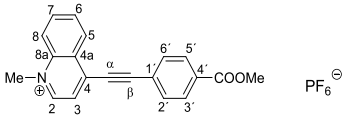
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.27 (d, *J* = 8.3 Hz, 1H, 4-H), 8.62 (d, *J* = 9.0 Hz, 1H, 8-H), 8.48 (d, *J* = 8.1 Hz, 1H, 3-H), 8.46 (d, *J* = 6.2 Hz, 1H, 5-H), 8.32 (ddd, *J* = 1.6, 7.2, 8.8 Hz, 1H, 7-H), 8.15 (d, *J* = 8.3 Hz, 2H, 3′-H, 5′-H), 8.10 (d, *J* = 8.3 Hz, 2H, 2′-H, 6′-H) 8.07 (t, *J* = 7.6 Hz, 1H, 6-H), 4.79 (s, 3H, NCH_3), 3.91 (s, 3H, COOCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.3 (o, *C*OO), 145.6 (+, C4), 140.3 (o, C2), 139.4 (o, C8a), 136.2 (+, C7), 133.4 (+, C2′, C6′), 132.2 (o,C4′), 130.3 (+, C5), 129.7 (+, C6, C3′, C5′), 128.6 (o, C4a), 126.3 (+, C3), 123.3 (o, C1′), 119.6 (+, C8), 106.5 (o, Cβ), 84.3 (o, Cα), 52.6 (+, O*C*H$_3$), 42.9 (+, N*C*H$_3$) ppm.

IR (ATR): 3099, 2209, 1716, 1619, 1596, 1578, 1523, 1478, 1442, 1431, 1406, 1354, 1287, 1162, 1106, 1060, 1020, 998, 959, 826, 771, 695, 601, 556, 500, 466, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ $[M]^+$ 302.1170, found 302.1174.

4-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate (42cPF$_6$)



According to **Procedure 5**, a solution of 0.036 g (0.088 mmol) of 4-((4 (methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate and 0.015 g (0.09 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) under rt to give 4-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate **42cPF$_6$**.

Yield: 0.038 g (97%) of a white-yellow solid.

Mp: 227 °C.

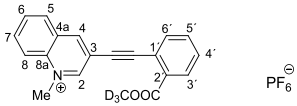
^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ = 9.52 (d, *J* = 6.2 Hz, 1H, 2-H), 8.78 (d, *J* = 8.2 Hz, 1H, 5-H), 8.57 (d, *J* = 8.2 Hz, 1H, 8-H), 8.41 (d, *J* = 6.2 Hz, 1H, 3-H), 8.35 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7-H), 8.16 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 6-H), 8.13–8.11 (m, 2H, 3′-H, 5′-H), 8.06–8.05 (m, 2H, 2′-H, 6′-H), 4.64 (s, 3H, NC*H*$_3$), 3.91 (s, 3H, COOC*H*$_3$) ppm.

^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ = 165.4 (o, *C*OO), 149.5 (+, C2), 138.4 (o, C8a), 137.9 (o, C4), 135.8 (+, C7), 133.1 (+, C2′, C6′), 130.9 (+, C6), 129.6 (+, C3′, C5′), 128.4 (o, C4a), 127.9 (+, C5), 124.6 (+, C3), 124.4 (o, C1′), 119.8 (+, C8), 105.2 (o, Cβ), 86.0 (o, Cα) 52.6 (+, COO*C*H$_3$), 45.5 (+, N*C*H$_3$) ppm.

IR (ATR): 3099, 2209, 1718, 1604, 1530, 1430, 1403, 1373, 1308, 1281, 1239, 1183, 1152, 1104, 1017, 997, 843, 822, 767, 692, 645, 589, 556, 532, 491, 465, 440 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ $[M]^+$ 302.1170, found 302.1178.

1-Methyl-3-((2-(((²H$_3$)methyloxy)carbonyl)phenyl)ethynyl)quinolinium hexafluorophosphate (48PF$_6$)



3-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **43** (0.171 g, 0.415 mmol) was dissolved in methanol-d_4 (5 mL) and then a 40% D_2O solution of sodium hydroxide (0.083 g) was added with stirring. The resulting mixture was stirred for 1 h. Then the solution was precipitated with a water solution of NH_4PF_6 (1 equiv), filtered, washed with water, diethyl ether, and dried *in vacuo*.

Yield: 0.185 g (99%) of a yellow solid.

Mp: 209 °C.

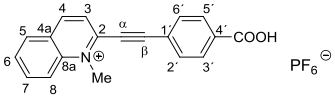
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.80 (d, *J* = 1.0 Hz, 1H, 2-H), 9.47 (s, 1H, 4-H), 8.54 (d, *J* = 9.1 Hz, 1H, 8-H), 8.50 (d, *J* = 9.1 Hz, 1H, 5-H), 8.32 (ddd, *J* = 1.5, 7.1, 9.1 Hz, 1H, 6-H), 8.11 (ddd, *J* = 1.5, 7.1, 9.1 Hz, 1H, 7-H), 8.04 (dd, *J* = 1.0, 8.0 Hz, 1H, 6′-H), 7.85 (dd, *J* = 1.0, 8.0 Hz, 1H, 3′-H), 7.76 (td, *J* = 1.5, 7.6 Hz, 1H, 4′-H), 7.66 (td, *J* = 1.5, 7.6 Hz, 1H, 5′-H), 4.66 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.5 (o, *C*OO), 151.9 (+, C2), 148.0 (+, C4), 137.4 (o, C8a), 136.1 (+, C7), 134.3 (+, C5′), 132.7 (+, C6′), 131.8 (o, C2′), 130.6 (+, C6), 130.5 (+, C4′), 130.4 (+, C5), 130.2 (+, C3′), 128.8 (o, C4a), 120.7 (o, C1′), 119.2 (+, C8), 116.8 (o, C3), 93.4 (o, Cα), 87.4 (o, Cβ), 52.5 (+, COO*C*D$_3$), 45.5 (+, N*C*H$_3$) ppm.

IR (ATR): 3361, 2220, 1736, 1604, 1594, 1571, 1518, 1493, 1379, 1353, 1257, 1219, 1199, 1133, 1081, 1035, 966, 924, 825, 764, 751, 698, 664, 622, 582, 555, 494, 434 cm^{-1}.

MS (ESI): *m/z* = 305.1 $[M]^+$.

2-((4-Carboxyphenyl)ethynyl)-1-methylquinolinium hexafluorophosphate (60bPF_6)



According to **Procedure 5**, a solution of 0.035 g (0.088 mmol) of 2 ((4-carboxyphenyl)ethynyl)-1-methylquinolinium methylsulfate **60b** and 0.015 g (0.09 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) under rt to give 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium hexafluorophosphate **42aPF_6**.

Yield: 0.038 g (97%) of a gray solid.

Mp: 186 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ =13.42 (br s, 1H, O*H*) 9.26 (d, *J* = 8.7 Hz, 1H, 4-H), 8.61 (d, *J* = 8.9 Hz, 1H, 8-H), 8.50 (d, *J* = 8.3 Hz, 1H, 5-H), 8.47 (d, *J* = 8.7 Hz, 1H, 3-H), 8.32 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 8.13 (d, *J* = 8.7 Hz, 2H, 3′-H, 5′-H), 8.07 (d, *J* = 8.5 Hz, 2H, 2′-H, 6′-H) 8.07 (t, *J* = 7.6 Hz, 1H, 6-H), 4.79 (s, 3H, NCH_3) ppm.

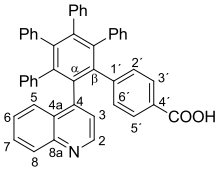
^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.4 (o, *C*OO), 145.6 (+, C4), 140.4 (o, C2), 139.4 (o, C8a), 136.2 (+, C7), 133.5 (o,C4′), 133.3 (+, C2′, C6′), 130.4 (+, C5), 129.7 (+, C6), 129.6 (+, C3′, C5′), 128.6 (o, C4a), 126.3 (+, C3), 122.8 (o, C1′), 119.6 (+, C8), 106.8 (o, Cβ), 84.1 (o, Cα), 42.9 (+, N*C*H_3) ppm.

IR (ATR): 2208, 1714, 1596, 1579, 1439, 1407, 1355, 1237, 1176, 1160, 1107, 1059, 1015, 1001, 827, 769, 752, 695, 557, 476 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO_2$ $[M]^+$ 288.1014, found 288.1039.

1-(Quinoline-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene (68)

Diphenyl ether (10 g) was melted in 50 mL round-bottomed flask fitted with an air condenser. 4-((Quinolin-4-yl)ethynyl)benzoic acid **66c** (0.137 g, 0.50 mmol) and tetraphenylcyclopentadienone **67** (0.240 g, 0.62 mmol) were added to the flask, which was heated for 4 h using a heat gun. The solution was cooled to rt. After cooling, *n*-hexane (50 mL) was added, resulting in the precipitation of a gray powder, which was collected by vacuum filtration, dissolved in ethyl acetate (3 × 20 mL), the solvent was removed afterward and the product was dried under vacuum.



Yield: 0.252 g (80%) of a yellow solid.

Mp: >330 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.81 (br s, 1H, COO*H*), 8.48 (d, *J* = 4.4 Hz, 1H, 2-H), 7.81 (d, *J* = 8.2 Hz, 1H, 5-H), 7.68 (d, *J* = 8.3 Hz, 1H, 8-H), 7.55 (ddd, *J* = 1.4, 6.9, 8.3 Hz, 1H, 7-H), 7.51 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1H, 6-H), 7.34 (dd, *J* = 1.7, 8.1 Hz, 1H, 3′-H), 7.31 (d, *J* = 4.4 Hz, 1H, 3-H), 7.14 (dd, *J* = 1.6, 8.1 Hz, 1H, 2′-H), 7.06 (dd, *J* = 1.7, 8.1 Hz, 1H, 5′-H), 7.02-6.98 (m, 4-H, Ph), 6.92 -6.80 (m, 14H, Ph), 6.80 (dd, *J* = 1.6, 8.1 Hz, 1H, 6′-H), 6.68-6,65 (m, 2H, Ph), 6.54-6.52 (m, 1H, Ph) ppm.

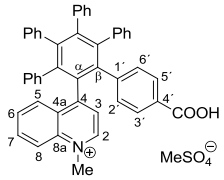
^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.8 (o, *C*OO), 148.6 (+, C2), 146.9 (o, C8a), 146.1 (o, C4), 144.1 (o, C1′), 141.0 (o), 140.6 (o), 140.1 (o), 139.9 (o), 139.6 (o), 139.5

(o), 139.3 (o), 139.08 (o), 139.12 (o, Cβ), 135.0 (o, Cα), 132.1 (+), 131.0 (+), 131.0 (+), 130.9 (+), 130.7 (+, C2′), 130.64 (+), 130.61 (+), 129.9 (+, C6′), 129.7 (+), 129.5 (+), 128.9 (+), 128.7 (+, C8), 127.9 (o, C4′), 127.3 (+, C3′), 127.1 (+, C5′), 126.9 (o, C4a), 126.73 (+), 126.68 (+), 126.64 (+), 126.59 (+, C5), 126.1 (+, C6), 125.8 (+), 125.7 (+), 125.6 (+), 124.3 (+, C3) ppm.

IR (ATR): 3055, 3025, 2920, 1791, 1695, 1602, 1586, 1506, 1496, 1442, 1403, 1372, 1236, 1215, 1173, 1100, 1072, 1042, 1017, 851, 813, 761, 696, 566, 553, 546, 502 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{46}H_{32}NO_2$ $[M+H]^+$ 630.2428, found 630.2429.

1-(1-Methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate (69)



According to **Procedure 3**, a solution of 0.100 g (0.160 mmol) of 1-(quinoline-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 1-(1-methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate **69**.

Yield: 0.115 (96%) of a yellow solid.

Mp: 204 °C (decomp.).

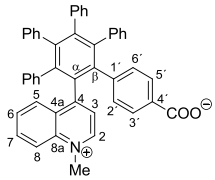
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.15 (d, *J* = 6.1 Hz, 1H, 2-H), 8.27 (d, *J* = 8.5 Hz, 1H, 5-H), 8.21 (d, *J* = 8.8 Hz, 1H, 8-H), 8.15 (d, *J* = 6.1 Hz, 1H, 3-H), 8.12 (ddd, *J* = 1.2, 7.3, 8.6 Hz, 1H, 7-H), 7.96 (t, *J* = 7.5 Hz, 1H, 6-H), 7.42 (dd, *J* = 1.6, 8.1 Hz, 1H, 3′-H), 7.21 (dd, *J* = 1.4, 8.1 Hz, 1H, 2′-H), 7.14 (dd, *J* = 1.6, 8.1 Hz, 1H, 5′-H), 7.06 (d, *J* = 7.9 Hz, 1H, Ph), 7.04-7.00 (m, 3H, Ph), 6.96-6.82 (m, 14H, 6′-H, Ph), 6.75-6.72 (m, 1H, Ph), 6.71-6.70 (m, 1H, Ph), 6.59 (t, *J* = 7.6 Hz, 1H, Ph) 4.41 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.7 (o, *C*OO), 157.9 (o, C4), 147.7 (+, C2), 143.1 (o, C1′), 142.4 (o), 141.0 (o), 139.5 (o), 139.2 (o), 138.9 (o), 138.7 (o), 138.5 (o, Cβ), 138.1 (o), 137.2 (o, C8a), 132.7 (o, Cα), 130.98 (+), 130.95 (+), 130.8 (+, C2′), 130.51 (+), 130.48 (+), 130.1 (+, C6′), 130.0 (+), 129.8 (+, C6), 129.2 (+, C5), 128.9 (o), 128.5 (o, C4′), 128.21 (o), 128.18 (o, C4a), 127.9 (+, C3′), 127.6 (+, C5′), 126.90 (+), 126.88 (+), 126.85 (+), 126.83 (+), 126.75 (+), 126.72 (+), 126.5 (+), 126.0 (+), 126.9 (+), 125.2 (+, C3), 118.9 (+, C8), 52.8 (+, *C*H_3SO_4), 45.1 (+, NCH_3) ppm.

IR (ATR): 3055, 2943, 1733, 1706, 1604, 1583, 1529, 1497, 1442, 1371, 1240, 1200, 1176, 1116, 1045, 1006, 911, 865, 817, 725, 698, 669, 609, 577, 556, 434 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{47}H_{34}NO_2$ $[M]^+$ 644.2585, found 644.2585.

1-(1-Methylquinolinium-4-yl)-2-(4-benzoate)-3,4,5,6-tetraphenylbenzene (70)



To a solution of 0.100 g (0.13 mmol) of 1-(1-methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate **69** in methanol (4 mL) was added

0.021 mL (0.15 mmol) of NEt_3. The resulting mixture was evaporated, the crude product washed with water, and dried *in vacuo* to give 1-(1-methylquinolinium-4-yl)-2-(4-benzoate)-3,4,5,6-tetraphenylbenzene **70**.

Yield: 0.073 g (88%) of a green solid.

Mp: 287 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[VII]: δ = 9.15 (d, *J* = 6.0 Hz, 1H, 2-H), 8.26 (dd, *J* = 0.9, 8.8 Hz, 1H, 5-H), 8.18 (d, *J* = 8.5 Hz, 1H, 8-H), 8.13 (d, *J* = 6.0 Hz, 1H, 3-H), 8.10 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H, 7-H), 7.96 (t, *J* = 7.7 Hz, 1H, 6-H), 7.33 (dd, *J* = 1.4, 8.0 Hz, 1H, 5′-H), 7.06-7.4 (m, 3H, 3′-H, 6′-H, Ph), 7.01-7.00 (m, 3H, Ph), 6.95-6.82 (m, 15H, Ph), 6.85[VIII] (m, 2′-H), 6.73 (d, *J* = 7.44 Hz, 1H, Ph), 6.71-6.69 (m, 2H, Ph), 6.58 (t, *J* = 7.6 Hz, 1H, Ph) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 167.8 (o, *C*OO), 158.8 (o, C4), 148.1 (+, C2), 142.8 (o), 141.2 (o), 141.0 (o, C1′), 139.9 (o), 139.8 (o), 139.7 (o), 139.4 (o), 139.3 (o), 138.7 (o, Cβ), 137.6 (o, C8a), 135.6 (+, C7), 133.4 (o, Cα), 131.5 (+), 131.3 (+), 131.0 (+, C6′), 130.5 (+, C2′), 130.4 (+, C6), 129.8 (+, C5), 128.7 (o, C4a), 128.1 (o, C3′), 127.9 (+, C5), 127.29 (+), 127.27 (+), 127.24 (+), 127.22 (+), 127.20 (+), 127.15 (+), 126.9 (+), 126.4 (+), 126.29 (+), 126.27 (+), 125.7 (+, C3), 119.4 (+, C8), 45.6 (+, N*C*H$_3$) ppm.

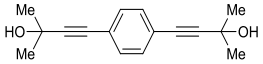
IR (ATR): 3053, 3026, 1713, 1601, 1527, 1496, 1441, 1368, 1227, 1173, 1016, 763, 727, 696, 554 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{47}H_{34}NO_2$ $[M+H]^+$ 644.2585, found 644.2581; $C_{47}H_{33}NNaO_2$ $[M+Na]^+$ 666.2404, found 666.2399.

[VII] All signals which are marked as "Ph" are belong to molecule (phenyl rest) but not possible to assign
[VIII] According to 2D spectra; C4′ was not possible to assign

5.3 Experiments to chapter 3.2.1 – 3.2.2

4,4'-Benzene-1,4-diylbis(2-methylbut-3-yn-2-ol) (74)



The reaction was carried out under a nitrogen atmosphere. A mixture of 20.00 mmol of 1,4-dibromobenzene **73**, 1 mol % of $Pd(PPh_3)_2Cl_2$, and 2 mol % of CuI were suspended in 20 mL of dry NEt_3 with stirring. A sample of MEBYNOL (3.0 equiv) in dry NEt_3 was added dropwise at ambient temperature. The resulting solution was then stirred at reflux temperature until complete conversion was monitored by TLC (3 h). Then the solvent was removed *in vacuo*. The resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.[IX]

Yield: 4.792 g (99%) of a white solid.

Mp: 159 °C.

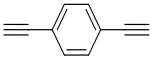
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (m, 4H, 2-H, 3-H, 5-H, 6-H), 2.04 (s, 2H, O*H*), 1.60 (s, 12H, CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.9 (+, C2, C3, C5, C6), 122.5 (o, C1, C4), 95.5 (*C*COH), 81.6 (*C*CCOH), 65.4 (*C*OH), 31.4 (+, *C*H_3) ppm.

IR (ATR): 3332, 2980, 2931, 1507, 1460, 1441, 1396, 1361, 1272, 1187, 1141, 959, 904, 846, 835, 789, 588, 562, 469 cm^{-1}.

[IX] Spectroscopic data are in agreement with those reported in the literature[96]

1,4-Diethynylbenzene (75)



According to **Procedure 2**, a solution of 3.630 g (15.00 mmol) of 4,4'-benzene-1,4-diylbis(2-methylbut-3-yn-2-ol), 0.882 g (15.75 mmol) of KOH and 3.339 g (15.75 mmol) of K_3PO_4 in 50 mL of anhydrous toluene was heated (0.25 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 1,4-diethynylbenzene **75**.[x]

Yield: 1.603 g (62%) of a white solid.

Mp: 93 °C.

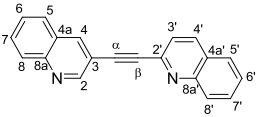
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 4H, 2-H, 3-H, 5-H, 6-H), 3.17 (s, 2H, CC*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.0 (+, C2, C3, C5, C6), 122.5 (o, C1, C4), 83.0 (o, *C*CH), 79.1 (o, C*C*H) ppm.

IR (ATR): 3260, 2104, 1919, 1668, 1506, 1495, 1404, 1368, 1251, 1170, 1105, 1016, 964, 905, 833, 675, 620, 545, 492 cm^{-1}.

[x] Spectroscopic data are in agreement with those reported in the literature[97]

2-((Quinolin-3-yl)ethynyl)quinoline (71a)



According to **Procedure 1** a solution of 0.163 g (1.00 mmol) of 2-chloroquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) CuI and 0.218 g (1.05 mmol) of 3-ethynylquinoline in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 2-((quinolin-3-yl)ethynyl)quinoline **71a**.

Yield: 0.107 g (38%) of an orange solid.

Mp: 137 °C (decomp.).

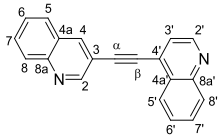
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.11 (d, *J* = 1.8 Hz, 1H, 2-H), 8.44 (s, 1H, 4-H), 8.16 (d, *J* = 8.5 Hz, 1H, 4′-H), 8.14 (d, *J* = 8.5 Hz, 1H, 8′-H), 8.11 (d, *J* = 8.5 Hz, 1H, 8-H), 7.82-7.80 (m, 2H, 5-H, 5′-H), 7.76-7.73 (m, 2H, 7-H, 7′-H), 7.65 (d, *J* = 8.5 Hz, 1H, 3′-H), 7.59-7.55 (m, 2H, 6-H, 6′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.2 (+, C2), 148.4 (o, C8a′), 147.3 (o, C8a), 143.1 (o, C2′), 139.6 (+, C4), 136.5 (+, C4′), 130.7 (+, C7), 130.4 (+, C7′), 129.6 (+, C8), 129.5 (+, C8′), 127.9 (+, C5), 127.7 (+, C5′), 127.6 (+, C6), 127.5 (+, C6′), 127.4 (o, C4a), 127.2 (o, C4a′), 124.4 (+, C3′), 116.4 (o, C3), 92.4 (o, Cβ), 87.0 (o, Cα) ppm.

IR (ATR): 2923, 2218, 2208, 1589, 1552, 1488, 1422, 1350, 1309, 1239, 1124, 1104, 1015, 985, 955, 908, 824, 786, 747, 635, 593, 551, 499, 470 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1074, found 281.1080.

3-(Quinolin-4-ylethynyl)quinoline (71b)



According to **Procedure 1**, a solution of 0.208 g (1.00 mmol) of 4-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) CuI and 0.218 g (1.05 mmol) of 3-ethynylquinoline in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(quinolin-4-ylethynyl)quinoline **71b**.

Yield: 0.160 g (57%) of a yellow solid.

Mp: 134 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.11 (d, *J* = 2.1 Hz, 1H, 2-H), 8.94 (d, *J* = 4.5 Hz, 1H, 2′-H), 8.45 (d, *J* = 2.0 Hz, 1H, 4-H), 8.40 (dd, *J* = 0.9, 8.3 Hz, 1H, 5′-H) 8.16 (d, *J* = 7.8, 1H, 8′-H), 8.14 (d, *J* = 7.8 Hz, 1H, 8-H) 7.85 (d, *J* = 7.9 Hz, 1H, 4-H), 7.80–7.76 (m, 2H, 7-H, 7′-H), 7.68 (ddd, *J* = 1.2, 6.9, 8.2 Hz, 1H, 6′-H), 7.63 (d, *J* = 4.3 Hz, 1H, 3′-H), 7.61 (ddd, *J* = 1.2, 7.1, 8.2 Hz, 1H, 6-H) ppm.

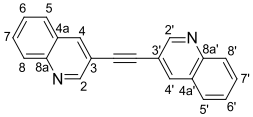
^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9 (+, C2), 149.9 (+, C2′), 148.3 (o, C8a′), 147.5 (o, C8a), 139.2 (+, C4), 130.9 (+, C7), 130.2 (+, C7′), 130.2 (+, C8′), 129.7 (+, C8), 129.1 (o, C4′), 127.9 (+, C5), 127.7 (+, C6), 127.6 (o, C4a′), 127.6 (+, C6′), 127.3 (o, C4a), 126.0 (+, C5′), 123.9 (+, C3′), 116.5 (o, C3), 95.7 (o, Cα), 88.3 (o, Cβ) ppm.

IR (ATR): 3033, 2209, 2203, 1615, 1572, 1484, 1419, 1282, 1220, 1192, 1123, 1011, 976, 905, 845, 787, 758, 651, 609, 542, 514, 491, 476, 445 cm^{-1}.

MS (ESI): *m/z* = 281.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1074, found 281.1062.

3,3'-Ethyne-1,2-diyldiquinoline (71c)



According to **Procedure 1**, a solution of 0.208 g (1.00 mmol) of 3-bromoquinoline **35**, 0.007 g (0.01 mmol) of $Pd(PPh_3)_2Cl_2$, 0.0038 g (0.02 mmol) CuI and 0.2184 g (1.05 mmol) of 3-ethynylquinoline in 10 mL of anhydrous NEt_3 was heated (2 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3,3'-ethyne-1,2-diyldiquinoline **71c**.

Yield: 0.196 g (70%) of a brownish solid.

Mp: 173 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.05 (d, *J* = 2 Hz, 2H, 2-H, 2′-H), 8.36 (d, *J* = 2 Hz, 2H, 4-H, 4′-H), 8.12 (d, *J* = 8.1 Hz, 2H, 8-H, 8′-H), 7.82 (d, *J* = 8.3 Hz, 2H, 5-H, 5′-H), 7.74 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 2H, 7-H, 7′-H) 7.58 (ddd, *J* = 1.1, 6.9, 8.0 Hz, 2H, 6-H, 6′-H) ppm.

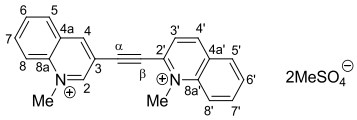
^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.0 (+, C2, C2′), 147.2 (o, C8a, C8a′), 138.8 (+, C4, C4′), 130.5 (+, C7, C7′), 129.6 (+, C8, C8′), 127.8 (+, C5, C5′), 127.6 (+, C6, C6′), 127.3 (o, C4a, C4a′), 116.9 (o, C3, C3′), 90.0 (o, Cα) ppm.

IR (ATR): 3061, 2169, 1839, 1616, 1565, 1487, 1468, 1413, 1357, 1291, 1226, 1192, 1122, 991, 955, 906, 878, 869, 786, 770, 761, 748, 737, 640, 614, 594, 553, 527, 491, 479, 472, 461, 445, 415 cm^{-1}.

MS (ESI): *m/z* = 281.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1074, found 281.1072.

1-Methyl-3-((1-methylquinolin-1-ium-2-yl)ethynyl)quinolin-1-ium dimethylsulfate (72a)



According to **Procedure 3**, a solution of 0.070 g (0.25 mmol) of 2-((quinolin-3-yl)ethynyl)quinoline, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 1-methyl-3-((1-methylquinolin-1-ium-2-yl)ethynyl)quinolin-1-ium dimethylsulfate **72a**.

Yield: 0.133 g (100%) of a dark violet solid.

Mp: 169 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.16 (s, 1H, 2-H), 9.89 (s, 1H, 4-H), 9.36 (d, *J* = 8.5 Hz, 1H, 4′-H), 8.69 (d, *J* = 8.8 Hz, 1H, 8-H), 8.64 (d, *J* = 8.8 Hz, 1H, 8′-H), 8.56 (d, *J* = 7.7 Hz, 1H, 5′-H), 8.52 (d, *J* = 8.2 Hz, 1H, 5-H), 8.50 (d, *J* = 8.5 Hz, 1H, 3′-H), 8.44 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7′-H), 8.37 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 8.19 (t, *J* = 7.1 Hz, 1H, 6′-H), 8.12 (t, *J* = 7.1 Hz, 1H, 6-H), 4.90 (s, 3H, N′CH_3), 4.72 (s, 3H, NCH_3), 3.36 (s, 6H, 2CH_3SO$_4$) ppm.

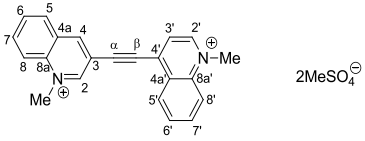
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.7 (+, C2), 150.9 (+, C4), 146.2 (+, C4′), 139.7 (o, C8a′), 139.5 (o, C2′), 138.4 (o, C4a), 137.7 (+, C7′), 136.5 (+, C7), 131.14 (+, C5′), 131.13 (+, C6′), 130.54 (+, C6), 130.48 (+, C5), 129.0 (o, C4a), 128.5 (o, C4a′),

119.8 (+, C8), 119.6 (+, C8′), 113.6 (o, C3), 100.4 (o, Cα), 85.9 (o, Cβ), 52.9 (+, *C*H_3SO_4), 45.8 (+, N*C*H_3), 43.3 (+, N′*C*H_3) ppm.

IR (ATR): 2946, 2832, 2225, 1595, 1520, 1456, 1380, 1356, 1214, 1057, 1043, 1001, 884, 836, 729, 659, 607, 575, 550, 500, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0736.

1-Methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dimethylsulfate (72b)



According to **Procedure 3**, a solution of 0.070 g (0.25 mmol) of 3-(quinolin-4-ylethynyl)quinoline, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 1-methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dimethylsulfate **72b**.

Yield: 0.126 g (95%) of a khaki colored solid.

Mp: 223 °C.

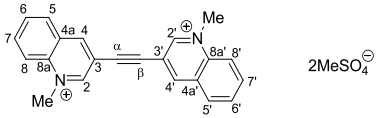
^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.16 (d, *J* = 0.9 Hz, 1H, 2-H), 9.86 (s, 1H, 4-H), 9.60 (d, *J* = 6.4 Hz, 1 H, 2′-H), 8.93 (dd, *J* = 1.0, 8.3 Hz, 5′-H), 8.63 (d, *J* = 8.8 Hz, 1H, 8′-H) 8.63 (d, *J* = 8.7 Hz, 1H, 8-H), 8.55 (d, *J* = 8.2 Hz, 1H, 5-H), 8.47 (d, *J* = 5.95 Hz, 3′-H) 8.43–8.39 (m, 2H, 7-H, 7′-H), 8.24 (ddd, *J* = 0.8, 7.14, 8.10 Hz, 1H, 6′-H), 8.18 (ddd, *J* = 0.7, 7.7, 8.0 Hz, 1H, 6-H), 4.73 (s, 3H, NCH_3), 4.69 (s, 3H, N′CH_3), 3.37 (s, 6H, 2CH_3SO_4) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.8 (+, C2), 150.3 (+, C4), 149.9 (+, C2′), 138.5 (o, C8a′), 138.1 (o, C8a), 137.3 (+, C7), 136.6 (o, C4′), 136.0 (+, C7′), 131.1 (+, C6′), 131.0 (+, C6), 130.9 (+, C5), 128.6 (o, C4a), 128.4 (o, C4a′), 127.8 (+, C5′), 125.0 (+, C3′), 120.1 (+, C8′), 119.6 (+, C8), 114.6 (o, C3), 99.1 (o, Cα), 87.9 (o, Cβ), 52.8 (+, 2*C*H$_3$SO$_4$), 45.7 (+, N*C*H$_3$), 45.7 (+, N′*C*H$_3$) ppm.

IR (ATR): 3040, 2219, 1604, 1527, 1435, 1402, 1371, 1331, 1222, 1143, 1058, 1003, 857, 770, 726, 702, 609, 577, 552, 507, 447, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0740.

3,3'-Ethyne-1,2-diylbis(1-methylquinolinium) dimethylsulfate (72c)



According to **Procedure 3**, a solution of 0.070 g (0.25 mmol) of 3,3'-ethyne-1,2-diyldiquinoline, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 3,3'-ethyne-1,2-diylbis(1-methylquinolinium) dimethylsulfate **72c**.

Yield: 0.133 g (100%) of a bone-colored solid.

Mp: 234 °C (decomp.).

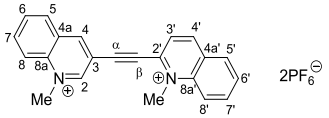
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.94 (d, *J* = 1 Hz, 2H, 2-H, 2′-H), 9.60 (s, 2H, 4-H, 4′-H), 8.60 (d, *J* = 8.8 Hz, 2H, 8-H, 8′-H), 8.54 (d, *J* = 8.3 Hz, 2H, 5-H, 5′-H), 8.38 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 2H, 7-H, 7′-H), 8.16 (t, *J* = 7.7 Hz, 2H, 6-H, 6′-H), 4.70 (s, 6H, N*C*H$_3$, N′*C*H$_3$), 3.37 (s, 6H, 2*C*H$_3$SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.1 (+, C2, C2′), 148.9 (+, C4, C4′), 137.9 (o, C8a, C8a′), 136.8 (+, C7, C7′), 130.9 (+, C6, C6′), 130.7 (+, C5, C5′), 128.7 (o, C4a, C4a′), 119.4 (+, C8, C8′), 115.2 (o, C3, C3′), 88.1 (o, Cα, Cβ), 52.9 (+, 2CH_3SO_4), 45.7 (+, NCH_3, N′CH_3) ppm.

IR (ATR): 3043, 2945, 1610, 1577, 1520, 1442, 1381, 1351, 1215, 1140, 1054, 1002, 873, 771, 730, 660, 608, 577, 554, 499, 456, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0716.

1-Methyl-3-((1-methylquinolin-1-ium-2-yl)ethynyl)quinolin-1-ium dihexafluorophosphate (72aPF_6)



According to **Procedure 5**, a solution of 0.025 g (0.047 mmol) of 1-methyl-3-((1-methylquinolin-1-ium-2-yl)ethynyl)quinolin-1-ium dimethylsulfate and 0.016 g (0.098 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) at rt to give 1-methyl-3-((1-methylquinolinium-2-yl)ethynyl)quinolinium dihexafluorophosphate.

Yield: 0.028 g (99%) of a dark violet solid.

Mp: 208 °C.

^{1}H NMR (600 MHz, DMSO-d_6)[XI]: δ = 10.16 (s, 1H, 2-H), 9.89 (s, 1H, 4-H), 9.36 (d, *J* = 8.5 Hz, 1H, 4′-H), 8.69 (d, *J* = 8.8 Hz, 1H, 8-H), 8.64 (d, *J* = 8.8 Hz, 1H, 8′-H), 8.56 (d, *J* = 7.7 Hz, 1H, 5′-H), 8.52 (d, *J* = 8.2 Hz, 1H, 5-H), 8.50 (d, *J* = 8.5 Hz, 1H, 3′-H),

[XI] The assignment was performed according to compound with methylsulfate anion

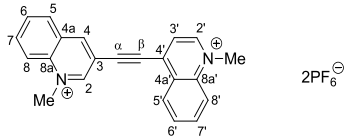
8.44 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7′-H), 8.37 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 8.19 (t, *J* = 7.1 Hz, 1H, 6′-H), 8.12 (t, *J* = 7.1 Hz, 1H, 6-H), 4.90 (s, 3H, N′C*H*$_3$), 4.72 (s, 3H, NC*H*$_3$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.7 (C2), 150.9 (C4), 146.2 (C4′), 139.7 (C8a′), 139.5 (C2′), 138.4 (C4a), 137.7 (C7′), 136.5 (C7), 131.14 (C5′), 131.13 (C6′), 130.54 (C6), 130.48 (C5), 129.0 (C4a), 128.5 (C4a′), 119.8 (C8), 119.6 (C8′), 113.6 (C3), 100.4 (Cα), 85.9 (Cβ), 45.8 (N*C*H$_3$), 43.3 (N′*C*H$_3$) ppm.

IR (ATR): 3098, 2224, 1600, 1581, 1522, 1381, 1358, 1314, 1253, 1235, 1166, 931, 829, 692, 557, 501, 485 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0732.

1-Methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dihexafluorophosphate (72bPF_6)



According to **Procedure 5**, a solution of 0.025 g (0.047 mmol) of 1-methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dimethylsulfate and 0.016 g (0.098 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) at rt to give 1-methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dihexafluorophosphate.

Yield: 0.028 g (99%) of an ivory solid.

Mp: 219 °C (decomp.).

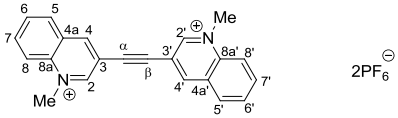
^{1}H NMR (600 MHz, DMSO-d_6)[XII]: δ = 10.16 (d, *J* = 0.9 Hz, 1H, 2-H), 9.86 (s, 1H, 4-H), 9.60 (d, *J* = 6.4 Hz, 1 H, 2′-H), 8.93 (dd, *J* = 1.0, 8.3 Hz, 5′-H), 8.63 (d, *J* = 8.8 Hz, 1H, 8′-H) 8.63 (d, *J* = 8.7 Hz, 1H, 8-H), 8.55 (d, *J* = 8.2 Hz, 1H, 5-H), 8.47 (d, *J* = 5.95 Hz, 3′-H) 8.43–8.39 (m, 2H, 7-H, 7′-H), 8.24 (ddd, *J* = 0.8, 7.14, 8.10 Hz, 1H, 6′-H), 8.18 (ddd, *J* = 0.7, 7.7, 8.0 Hz, 1H, 6-H), 4.73 (s, 3H, NCH_3), 4.69 (s, 3H, N′CH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.8 (C2), 150.3 (C4), 149.9 (C2′), 138.5 (C8a′), 138.1 (C8a), 137.3 (C7), 136.6 (C4′), 136.0 (C7′), 131.1 (C6′), 131.0 (C6), 130.9 (C5), 128.6 (C4a), 128.4 (C4a′), 127.8 (C5′), 125.0 (C3′), 120.1 (C8′), 119.6 (C8), 114.6 (C3), 99.1 (Cα), 87.9 (Cβ), 45.7 (N1CH_3), 45.7 (N1′CH_3) ppm.

IR (ATR): 3102, 2222, 1619, 1606, 1575, 1524, 1405, 1378, 1326, 1239, 1180, 1145, 1115, 930, 827, 768, 556 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0726.

3,3'-(Ethyne-1,2-diyl)bis(1-methylquinolin-1-ium) dihexafluorophosphate (72cPF_6)



According to **Procedure 5**, a solution of 0.025 g (0.047 mmol) of 3,3'-(ethyne-1,2-diyl)bis(1-methylquinolin-1-ium) dimethylsulfate and 0.016 g (0.098 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred (0.5 h) at rt to give 3,3'-(ethyne-1,2-diyl)bis(1-methylquinolin-1-ium) dihexafluorophosphate.

Yield: 0.028 g (99%) of an ivory solid.

[XII] The assignment was performed according to compound with methylsulfate anion

Mp: 261 °C (decomp.).

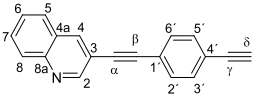
^{1}H NMR (600 MHz, DMSO-d_6)[XIII]: δ = 9.94 (d, *J* = 1 Hz, 2H, 2-H, 2′-H), 9.60 (s, 2H, 4-H, 4′-H), 8.60 (d, *J* = 8.8 Hz, 2H, 8-H, 8′-H), 8.54 (d, *J* = 8.3 Hz, 2H, 5-H, 5′-H), 8.38 (ddd, *J* = 1.5, 7.1, 8.6 Hz, 2H, 7-H, 7′-H), 8.16 (t, *J* = 7.7 Hz, 2H, 6-H, 6′-H), 4.70 (s, 6H, 2NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.1 (C2, C2′), 148.9 (C4, C4′), 137.9 (C8a, C8a′), 136.8 (C7, C7′), 130.9 (C6, C6′), 130.7 (C5, C5′), 128.7 (C4a, C4a′), 119.4 (C8, C8′), 115.2 (C3, C3′), 88.1 (Cα, Cβ), 45.7 (NCH_3, N′CH_3) ppm.

IR (ATR): 3101, 1608, 1520, 1451, 1380, 1348, 1212, 1140, 1113, 1041, 975, 930, 822, 768, 659, 623, 556, 494, 455, 427 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0731.

3-((4-Ethynylphenyl)ethynyl)quinoline (78)



According to **Procedure 1**, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI and 1.197 g (9.50 mmol) of 1,4-diethynylbenzene in 50 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-((4-ethynylphenyl)ethynyl)quinoline **78**.

Yield 0.889 g (37%) of a brown solid.

[XIII] The assignment was performed according to compound with methylsulfate anion

Mp: 113 °C.

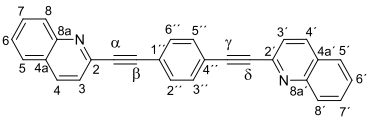
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.99 (d, *J* = 2.1 Hz, 1H, 2-H), 8.30 (d, *J* = 2.1 Hz, 1H, 4-H), 8.10 (d, *J* = 8.5 Hz, 1H, 8-H), 7.70 (d, *J* = 8.1 Hz, 1H, 5-H), 7.73 (ddd, *J* = 1.5, 7.0, 8.5 Hz, 1H, 7-H), 7.57 (ddd, *J* = 1.5, 7.0, 8.1 Hz, 1H, 6-H), 7.55-7.53 (m, 2H, 2′-H, 6′-H), 7.51-7.49 (m, 2H, 3′-H, 5′-H), 3.20 (s, 1H, CC*H*) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (+, C2), 147.1 (o, C8a), 138.5 (+, C4), 132.3 (+, C3′, C5′), 131.7 (+, C2′, C6′), 130.4 (+, C7), 129.6 (+, C8), 127.8 (+, C5), 127.5 (+, C6), 127.4 (o, C4a), 123.2 (o, C1′), 122.6 (o, C4′), 117.2 (o, C3), 92.1 (o, Cβ), 88.7 (o, Cα), 83.2 (o, Cγ), 79.4 (o, Cδ) ppm.

IR (ATR): 3265, 3060, 3034, 2101, 1969, 1710, 1699, 1602, 1566, 1487, 1404, 1351, 1266, 1145, 1105, 1010, 981, 958, 906, 861, 838, 782, 752, 691, 653, 622, 548, 471, 419 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{19}H_{12}N$ $[M+H]^+$ 254.0964, found 254.0972; *m/z* calcd for $C_{19}H_{11}NNa$ $[M+Na]^+$ 276.0789, found 276.0785.

2,2'-(Benzene-1,4-diyldiethyne-2,1-diyl)diquinoline (76a)



According to **Procedure 1**, a solution of 0.408 g (2.50 mmol) of 2-chloroquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 2,2'-(benzene-1,4-diyldiethyne-2,1-diyl)diquinoline **76a**.

Yield: 0.209 g (55%) of a yellow solid.

Mp: 207 °C.

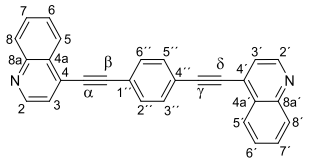
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.1 Hz, 2H, 4-H, 4′-H), 8.13 (d, *J* = 7.9 Hz, 2H, 8-H, 8′-H), 7.80 (d, *J* = 8.1 Hz, 2H, 5-H, 5′-H), 7.74 (ddd, *J* = 1.4, 6.8, 7.9 Hz, 2H, 7-H, 7′-H), 7.66 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 7.60 (d, *J* = 8.1 Hz, 3-H, 3′-H), 7.55 (ddd, *J* = 1.4, 6.8, 8.1 Hz, 2H, 6-H, 6′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.3 (o, C8a, C8a′), 143.3 (o, C2, C2′), 136.3 (+, C4, C4′), 132.2 (+, C2″, C3″, C5″, C6″), 130.2 (+, C7, C7′), 129.4 (+, C8, C8′), 127.6 (+, C5, C5′), 127.3 (+, C6, C6′), 127.2 (o, C4a, C4a′), 124.4 (+, C3, C3′), 122.9 (o, C1″, C4″), 91.4 (o, Cα, Cδ), 89.3 (o, Cβ, Cγ) ppm.

IR (ATR): 3056, 2211, 2186, 1590, 1548, 1505, 1419, 1289, 1107, 971, 950, 830, 790, 748, 629, 555, 480 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{28}H_{16}N_2$ $[M+H]^+$ 381.1386, found 381.1390.

4,4'-(Benzene-1,4-diyldiethyne-2,1-diyl)diquinoline (76b)



According to **Procedure 1**, a solution of 0.520 g (2.50 mmol) of 4-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) CuI and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 4,4'-(benzene-1,4-diyldiethyne-2,1-diyl)diquinoline **76b**.

Yield: 0.103 g (27%) of an orange solid.

Mp: 225 °C (decomp.).

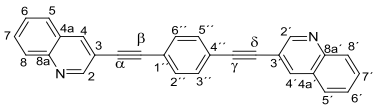
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 4.4 Hz, 2H, 2-H, 2′-H), 8.37 (ddd, *J* = 0.5, 1.4, 8.3 Hz, 2H, 5-H, 5′-H), 8.15 (ddd, *J* = 0.5, 1.3, 8.5 Hz, 2H, 8-H, 8′-H), 7.79 (ddd, *J* = 1.3, 6.9, 8.4 Hz, 2H, 7-H, 7′-H), 7.72 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 7.67 (ddd, *J* = 1.3, 6.9, 8.4 Hz, 2H, 6-H, 6′-H), 7.59 (d, *J* = 4.4 Hz, 2H, 3-H, 3′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.9 (+, C2, C2′), 148.3 (o, C8a, C8a′), 132.2 (+, C2″, C3″, C5″, C6″), 130.2 (+, C8, C8′), 130.1 (+, C7, C7′), 129.4 (o, C4, C4′), 127.7 (o, C4a, C4a′), 127.5 (+, C6, C6′), 126.0 (+, C5, C5′), 123.8 (+, C3, C3′), 123.3 (o, C1″, C4″), 98.0 (o, Cβ, Cγ), 87.5 (o, Cα, Cδ) ppm.

IR (ATR): 2981, 1733, 1576, 1561, 1506, 1495, 1461, 1435, 1389, 1361, 1272, 1154, 1134, 1102, 1027, 961, 904, 868, 846, 759, 722, 691, 642, 625, 571, 547, 470, 442 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{28}H_{16}N_2$ $[M+H]^+$ 381.1386, found 381.1390.

3,3'-(Benzene-1,4-diyldiethyne-2,1-diyl)diquinoline (76c)



According to **Procedure 1**, a solution of 0.520 g (2.50 mmol) of 3-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) CuI and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3,3'-(Benzene-1,4-diyldiethyne-2,1-diyl)diquinoline **76c**.

Yield: 0.095 g (25%) of a yellow solid.

Mp: 203 °C.

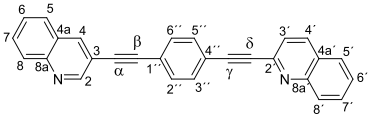
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 2.0 Hz, 2H, 2-H, 2′-H), 8.32 (d, *J* = 2.0 Hz, 2H, 4-H, 4′-H), 8.11 (d, *J* = 8.1 Hz, 2H, 8-H, 8′-H), 7.81 (d, *J* = 7.7 Hz, 2H, 5-H, 5′-H), 7.73 (ddd, *J* = 1.5, 7.0, 8.1 Hz, 2H, 7-H, 7′-H), 7.60 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 7.58 (ddd, *J* = 1.5, 7.0. 7.7 Hz, 2H, 6-H, 6′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (+, C2, C2′), 147.1 (o, C8a, C8a′), 138.5 (+, C4, C4′), 131.9 (+, C2″, C3″, C5″, C6″), 130.4 (+, C7, C7′), 129.6 (+, C8, C8′), 127.8 (+, C5, C5′), 127.5 (+, C6, C6′), 127.4 (o, C4a, C4a′), 123.1 (o, C1″, C4″), 117.3 (o, C3, C3′), 92.3 (o, Cβ, Cγ), 88.9 (o, Cα, Cδ) ppm.

IR (ATR): 3066, 3055, 3016, 1838, 1567, 1486, 1354, 1101, 981, 958, 906, 863, 830, 785, 746, 641, 620, 569, 547, 516, 474, 459, 432 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{28}H_{16}N_2$ $[M+H]^+$ 381.1386, found 381.1387.

2-((4-(Quinolin-3-ylethynyl)phenyl)ethynyl)quinoline (76d)



According to **Procedure 1**, a solution of 0.017 g (0.11 mmol) of 2-chloroquinoline, 0.007 g (0.01 mmol) of $Pd(PPh_3)_2Cl_2$, 0.0038 g (0.02 mmol) of CuI and 0.030 g (0.12 mmol) of 3-((4-ethynylphenyl)ethynyl)quinoline in 10 mL of anhydrous NEt_3 was heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 2-((4-(quinolin-3-ylethynyl)phenyl)ethynyl)quinoline **76d**.

Yield: 0.035 g (81%) of a yellow solid.

Mp: 197 °C.

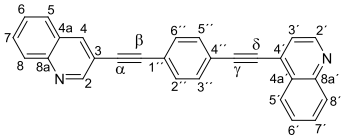
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.01 (s, 1H, 2-H), 8.32 (d, *J* = 1.9 Hz, 1H, 4-H), 8.16-8.13 (m, 2H, 4′-H, 8′-H), 7.81-7.80 (m, 2H, 5-H, 5′-H), 7.76-7.72 (m, 2H, 7-H, 7′-H), 7.68-7.67 (m, 2H, 3″-H, 5″-H), 7.61 (d, *J* = 8.5 Hz, 1H, 3′-H), 7.60-7.59 (m, 2H, 2″-H, 6″-H), 7.58-7.54 (m, 2H, 6-H, 6′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (+, C2), 148.4 (o, C8a′), 147.0 (o, C8a), 143.4 (o, C2′), 138.6 (+, C4), 136.4 (+, C4′), 132.4 (+, C3″, C5″), 131.9 (+, C2″, C6″), 130.4 (+, C7), 130.3 (+, C7′), 129.54 (+, C8), 129.49 (+, C8′), 127.8 (+, C5), 127.7 (+, C5′), 127.5 (+, C6), 127.41 (+, C6′), 127.37 (o, C4a), 127.3 (o, C4a′), 124.5 (+, C3′), 123.5 (o, C1″), 122.6 (o, C4″), 117.3 (o, C3), 92.3 (o, Cβ), 91.4 (o, Cδ), 89.4 (o, Cγ), 89.0 (o, Cα) ppm.

IR (ATR): 3051, 3037, 2958, 2922, 2851, 2210, 1738, 1733, 1615, 1593, 1550, 1488, 1460, 1405, 1352, 1342, 1306, 1288, 1242, 1158, 1115, 1106, 1046, 1012, 980, 955, 912, 871, 850, 828, 790, 748, 693, 626, 613, 552, 520, 472, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{28}H_{16}N_2$ $[M+H]^+$ 381.1386, found 381.1382.

3-((4-(Quinolin-4-ylethynyl)phenyl)ethynyl)quinoline (76e)



According to **Procedure 1**, a solution of 0.208 g (1.00 mmol) of 4-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI and 0.278 g (1.10 mmol) of 3-((4-ethynylphenyl)ethynyl)quinoline in 25 mL of anhydrous NEt_3 was

heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-((4-(quinolin-4-ylethynyl)phenyl)ethynyl)quinoline **76e**.

Yield: 0.228 g (60%) of a yellow solid.

Mp: 153 °C.

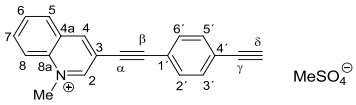
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.02 (d, *J* = 2.1 Hz, 1H, 2-H), 8.92 (d, *J* = 4.3 Hz, 1H, 2-H′), 8.37 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.33 (s, 1H, 4-H), 8.16 (d, *J* = 8.1 Hz, 1H, 8′-H), 8.12 (d, *J* = 8.5 Hz, 1H, 8-H), 7.81 (d, *J* = 7.9 Hz, 1H, 5-H), 7.80-7.77 (m, 1H, 7′-H), 7.76-7.73 (m, 1H, 7-H), 7.68 (d, *J* = 8.3 Hz, 2H, 3″-H, 5″-H), 7,67-7.65 (m, 1H, 6′-H), 7.64 (d, *J* = 8.3 Hz, 2H, 2″-H, 6″-H), 7.60-7.57 (m, 2H, 6-H, 3′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (+, C2), 149.7 (+, C2′), 148.0 (o, C8a′), 147.1 (o, C8a), 138.6 (+, C4), 132.2 (+, C3″, C5″), 132.0 (+, C2″, C6″), 130.5 (+, C7), 130.3 (+, C7′), 129.9 (+, C8′), 129.7 (o, C4′), 129.6 (+, C8), 127.81 (+, C5), 127.76 (o, C4a′), 127.57 (+, C6), 127.54 (+, C6′), 127.36 (o, C4a), 126.1 (+, C5), 123.78 (o, C1″), 123.75 (+, C3′), 122.6 (o, C4″), 117.2 (o, C3), 98.4 (o, Cγ), 92.2 (o, Cβ), 89.3 (o, Cα), 87.2 (o, Cδ) ppm.

IR (ATR): 3033, 2210, 2188, 1733, 1575, 1511, 1486, 1462, 1418, 1393, 1351, 1294, 1194, 1101, 1012, 981, 954, 906, 864, 829, 782, 746, 678, 641, 592, 543, 476, 463, 419 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{28}H_{16}N_2$ $[M+H]^+$ 381.1386, found 381.1384.

3-((4-Ethynylphenyl)ethynyl)-1-methylquinolinium methylsulfate



According to **Procedure 3**, a solution of 0.127 g (0.50 mmol) of 3-((4-ethynylphenyl)ethynyl)quinoline, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 3-((4-ethynylphenyl)ethynyl)-1-methylquinolinium methylsulfate.

Yield: 0.176 g (93%) of a yellow solid.

Mp: 183 °C (decomp.).

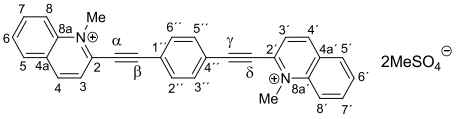
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.87 (dd, *J* = 0.7, 1.7 Hz, 1H, 2-H), 9.50 (s, 1H, 4-H), 8.54 (dd, *J* = 0.7, 8.9 Hz, 1H, 8-H), 8.45-8.44 (m, 1H, 5-H), 8.31 (ddd, *J* = 1.5, 7.1, 8.9 Hz, 1H, 7-H), 8.10 (ddd, *J* = 0.8, 7.1, 8.1 Hz, 1H, 6-H), 7.70-7.68 (m, 2H, 2′-H, 6′-H), 7.64-7.62 (m, 2H, 3′-H, 5′-H), 4.65 (s, 3H, NCH_3), 4.47 (s, 1H, CC*H*), 3.37 (s, 3H, CH_3SO_4) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (+, C2), 148.1 (+, C4), 137.4 (o, C8a), 136.2 (+, C7), 132.3 (+, C3′, C5′), 132.0 (+, C2′, C6′), 130.6 (+, C6), 130.4 (+, C5), 128.7 (o, C4a), 123.3 (o, C4′), 120.9 (o, C1′), 119.3 (+, C8), 116.5 (o, C3), 94.0 (o, Cβ), 85.1 (o, Cα), 83.7 (+, Cδ), 82.7 (+, Cγ), 52.8 (+, CH_3SO_4), 45.5 (+, NCH_3) ppm.

IR (ATR): 3218, 3048, 2944, 2223, 2103, 1677, 1607, 1583, 1522, 1503, 1453, 1378, 1366, 1320, 1227, 1173, 1139, 1060, 1011, 919, 851, 839, 772, 745, 609, 578, 552, 485, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{20}H_{14}N$ $[M]^+$ 268.1121, found 268.1117.

2,2'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate (77a)



According to **Procedure 3**, a solution of 0.048 g (0.125 mmol) of 2,2'-(benzene-1,4-diyldiethyne-2,1-diyl)diquinoline, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 2,2'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate **77a**.

Yield: 0.079g (99%) of a yellow solid.

Mp: 241 °C (decomp).

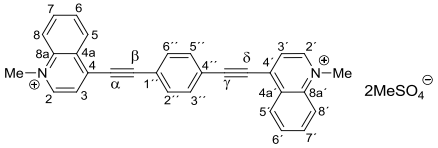
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.28 (d, *J* = 8.6 Hz, 2H, 4-H, 4′-H), 8.63 (d, *J* = 8,8 Hz, 2H, 8-H, 8′-H), 8.49 (d, *J* = 8.3 Hz, 2H, 3-H, 3′-H), 8.48 (d, *J* = 7.5 Hz, 2H, 5-H, 5′-H), 8.33 (t, *J* = 7,7 Hz, 2H, 7-H, 7′-H), 8.19 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 8.07 (t, *J* = 7.5 Hz, 2H, 6-H, 6′-H), 4.81 (s, 6H, NCH_3), 3.37 (s, 6H, CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 145.7 (+, C4, C4′), 140.3 (o, C2, C2′), 139.4 (o, C8a, C8a′), 136.2 (+, C7, C7′), 133.6 (+, C2″, C3″, C5″, C6″), 130.4 (+, C5, C5′), 130.2 (+, C6, C6′), 128.7 (o, C4a, C4a′), 126.4 (+, C3, C3′), 122.1 (o, C1″, C4″), 119.6 (+, C8, C8′), 106.6 (o, Cβ, Cγ), 85.1 (o, Cα, Cδ), 52.8 (+, 2CH_3SO$_4$), 43.0 (+, NCH_3, N′CH_3) ppm.

IR (ATR): 3070, 2203, 1615, 1594, 1575, 1521, 1437, 1353, 1160, 1045, 1000, 838, 744, 576, 553, 498, 476, 428 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ [M]$^{2+}$ 205.0884, found 205.0889.

4,4'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate 77b



According to **Procedure 3**, a solution of 0.048 g (0.125 mmol) of 4,4'-(benzene-1,4-diyldiethyne-2,1-diyl)diquinoline, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 4,4'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate **77b**.

Yield: 0.075 g (93%) of a yellow solid.

Mp: 218 °C (decomp.).

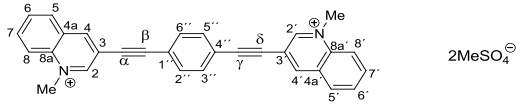
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.52 (d, *J* = 6.0 Hz, 2H, 2-H, 2-H′), 8.80 (d, *J* = 8.3 Hz, 2H, 5-H, 5′-H), 8.57 (d, *J* = 8.8 Hz, 2H, 8-H, 8′-H), 8.40 (d, *J* = 6.0 Hz, 2H, 3-H, 3′-H), 8.35 (t, *J* = 7.8 Hz, 2H, 7-H, 7′-H), 8.16 (t, *J* = 7.5 Hz, 2H, 6-H, 6′-H), 8.12 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 4.64 (s, 6H, NCH_3, N′CH_3), 3.38 (s, 6H, 2CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 149.5 (+, C2, C2′), 138.4 (o, C8a, C8a′), 137.8 (o, C4, C4′), 135.8 (+, C7, C7′), 133.4 (+, C2″, C3″, C5″, C6″), 130.9 (+, C6, C6′), 128.3 (+, C5, C5′), 127.9 (o, C4a, C4a′), 124.6 (+, C3, C3′), 122.5 (o, C1″, C4″), 119.8 (+, C8a, C8a′), 105.6 (o, Cβ, Cγ), 86.6 (o, Cα, Cδ), 52.8 (+, 2CH_3SO$_4$), 45.5 (+, NCH_3, N′CH_3) ppm.

IR (ATR): 3067, 3015, 2948, 2207, 1601, 1565, 1528, 1401, 1371, 1325, 1216, 1149, 1120, 1110, 1055, 994, 856, 807, 775, 738, 708, 646, 608, 577, 553, 488, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ [M]$^{2+}$ 205.0884, found 205.0885.

3,3'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate (77c)



According to **Procedure 3**, a solution of 0.048 g (0.125 mmol) of 3,3'-(benzene-1,4-diyldiethyne-2,1-diyl)diquinoline, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 3,3'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate **77c**.

Yield: 0.078 g (99%) of a yellow solid.

Mp: 265 °C (decomp.).

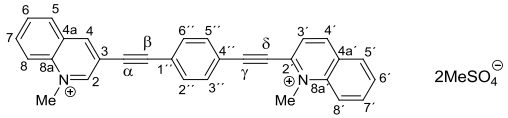
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.89 (d, *J* = 1.0 Hz, 2H, 2-H, 2′-H), 9.53 (s, 2H, 4-H, 4′-H), 8.55 (d, *J* = 8.9 Hz, 2H, 8-H, 8′-H), 8.47 (d, *J* = 7.5 Hz, 2H, 5-H, 5′-H), 8.33 (ddd, *J* = 1.6, 7.1, 8.7 Hz, 2H, 7-H, 7′-H), 8.11 (t, *J* = 7.9 Hz, 2H, 6-H, 6′-H), 7.83 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 4.67 (s, 6H, 2NCH_3), 3.37 (s, 6H, 2CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (+, C2, C2′), 148.2 (+, C4, C4′), 137.4 (o, C8a, C8a′), 136.3 (+, C7, C7′), 132.3 (+, C2″, C3″, C5″, C6″), 130.7 (+, C6, C6′), 130.4 (+, C5, C5′) 128.7 (o, C4a, C4a′), 122.1 (o, C1″, C4″), 119.3 (+, C8, C8′), 116.4 (o, C3, C3′), 93.9 (o, Cβ, Cγ), 85.8 (o, Cα, Cδ),52.8 (+, 2CH_3SO$_4$), 45.5 (+, NCH_3, N′CH_3) ppm.

IR (ATR): 3045, 2219, 1629, 1605, 1580, 1520, 1448, 1378, 1358, 1214, 1168, 1140, 1057, 1002, 920, 846, 773, 733, 609, 576, 552, 432 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0881.

1-Methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)quinolinium dimethylsulfate (77d)



According to **Procedure 3**, a solution of 0.048 g (0.125 mmol) of 2-((4-(quinolin-3-ylethynyl)phenyl)ethynyl)quinoline, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated over the period of 3 h under reflux temperature to give 1-methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)quinolinium dimethylsulfate **77d**.

Yield: 0.078 g (99%) of a yellow solid.

Mp: 205 °C (decomp.).

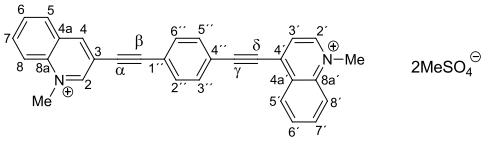
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.91 (d, *J* = 0.9 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.26 (d, *J* = 8.6 Hz, 1H, 4′-H), 8.62 (d, *J* = 8.9 Hz, 1H, 8′-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.48-8.46 (m, 3H, 5-H, 3′-H, 5′-H), 8.36-8.31 (m, 2H, 7-H, 7′-H), 8.14-8.11 (m, 3H, 6-H, 3″-H, 5″-H), 8.07 (t, *J* = 7.6 Hz, 1H, 6′-H), 7.91 (d, *J* = 8.4 Hz, 2H, 2″-H, 6″-H), 4.80 (s, 3H, N′CH_3), 4.67 (s, 3H, NCH_3), 3.37 (s, 6H, 2CH_3SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (+, C2), 148.3 (+, C4), 145.6 (+, C4′), 140.2 (o, C2′), 139.4 (o, C8a′), 137.5 (o, C8a), 136.4 (+, C7), 136.2 (+, C7′), 133.6 (+, C3″, C5″), 132.4 (+, C2″, C6″), 130.7 (+, C6), 130.44 (+, C5 or C5′), 130.37 (+, C5 or C5′), 130.2 (+, C6′), 128.7 (o, C4a), 128.6 (o, C4a′), 126.3 (+, C3′), 124.1 (o, C1′), 120.1 (o, C4′), 119.6 (+, C8′), 119.3 (+, C8), 116.2 (o, C3), 107.1 (o, Cγ), 93.6 (o, Cβ), 86.8 (o, Cα), 84.6 (o, Cδ), 52.8 (+, 2CH_3SO$_4$), 45.5 (+, NCH_3), 42.9 (+, N′CH_3) ppm.

IR (ATR): 3049, 2200, 1594, 1575, 1520, 1455, 1437, 1408, 1377, 1354, 1307, 1216, 1155, 1056, 1001, 838, 735, 609, 577, 552, 497, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0886.

1-Methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl))quinolinium dimethylsulfate (77e)



According to **Procedure 3**, a solution of 0.048 g (0.125 mmol) of 3-((4-(quinolin-4-ylethynyl)phenyl)ethynyl)quinoline, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated over the period of 3 h under reflux temperature to give 1-methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl))quinolinium dimethylsulfate **77e**.

Yield: 0.078 g (99%) of a yellow solid.

Mp: 259 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.91 (d, *J* = 1.0 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.53 (d, *J* = 6.4 Hz, 1H, 2′-H), 8.81 (d, *J* = 9.0 Hz, 1H, 5′-H), 8.58 (d, *J* = 9.0 Hz, 1H, 8′-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.47 (d, *J* = 7.8 Hz, 1H, 5-H), 8.37-8.32 (m, 2H, 7-H, 7′-H), 8.17 (t, *J* = 7.5 Hz, 1H, 6′-H), 8.12 (t, *J* = 7.5 Hz, 1H, 6-H), 8.09 (d, *J* = 8.3 Hz, 2H, 3′′-H, 5′′-H), 7.89 (d, *J* = 8.3 Hz, 2H, 2′′-H, 6′′-H), 4.67 (s, 3H, NCH_3), 4.64 (s, 3H, N′CH_3), 3.37 (s, 6H, 2C$H_3$$SO_4$) ppm.

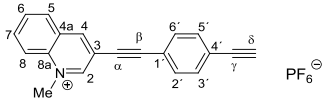
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (+, C2), 149.5 (+, C2′), 148.3 (+, C4), 138.4 (o, C8a′), 138.0 (o, C4′), 137.5 (o, C8a), 136.3 (+, C7), 135.8 (+, C7′), 133.4 (+, C3′′, C5′′), 132.3 (+, C2′′, C6′′), 130.9 (+, C6′), 130.7 (+, C6), 130.4 (+, C5), 128.7 (o, C4a), 128.4 (o, C4a′), 127.9 (+, C5′), 124.4 (+, C3′), 123.3 (o, C1′′), 121.3 (o, C4′′),

119.9 (+, C8′), 119.3 (+, C8), 116.3 (o, C3), 105.8 (o, Cγ), 93.8 (o, Cβ), 86.4 (o, Cα), 86.2 (o, Cδ), 52.8 (+, 2*C*H$_3$SO$_4$), 45.5 (+, NC*H*$_3$), 45.4 (+, N′C*H*$_3$) ppm.

IR (ATR): 3083, 3049, 2945, 2203, 2162, 1604, 1569, 1520, 1405, 1372, 1326, 1244, 1226, 1214, 1058, 1011, 904, 844, 771, 737, 609, 575, 552, 500, 486, 465, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0885.

3-((4-Ethynylphenyl)ethynyl)-1-methylquinolinium hexafluorophosphate



According to **Procedure 5**, a solution of 0.050 g (0.133 mmol) of 3-((4-ethynylphenyl)ethynyl)-1-methylquinolinium methylsulfate and 0.023 g (0.140 mmol) of NH_4PF_6 in 4 mL of water was stirred over the period of 0.5 h at rt to give 3-((4-ethynylphenyl)ethynyl)-1-methylquinolinium hexafluorophosphate.

Yield: 0.050 g (91%) of a yellow solid.

Mp: 233 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-*d*$_6$)[XIV]: δ = 9.87 (dd, *J* = 0.7, 1.7 Hz, 1H, 2-H), 9.50 (s, 1H, 4-H), 8.54 (dd, *J* = 0.7, 8.9 Hz, 1H, 8-H), 8.45-8.44 (m, 1H, 5-H), 8.31 (ddd, *J* = 1.5, 7.1, 8.9 Hz, 1H, 7-H), 8.10 (ddd, *J* = 0.8, 7.1, 8.1 Hz, 1H, 6-H), 7.70-7.68 (m, 2H, 2′-H, 6′-H), 7.64-7.62 (m, 2H, 3′-H, 5′-H), 4.65 (s, 3H, NCH$_3$), 4.47 (s, 1H, CC*H*) ppm.

^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ = 152.2 (+, C2), 148.1 (+, C4), 137.4 (o, C8a), 136.2 (+, C7), 132.3 (+, C3′, C5′), 132.0 (+, C2′, C6′), 130.6 (+, C6), 130.4 (+, C5),

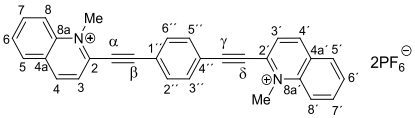
[XIV] The assignment was performed according to compound with methylsulfate anion

128.7 (o, C4a), 123.3 (o, C4′), 120.9 (o, C1′), 119.3 (+, C8), 116.5 (o, C3), 94.0 (o, Cβ), 85.1 (o, Cα), 83.7 (+, Cδ), 82.7 (+, Cγ), 45.5 (+, N*C*H$_3$) ppm.

IR (ATR): 3278, 3096, 2222, 1608, 1581, 1523, 1502, 1381, 1357, 1319, 1223, 923, 827, 768, 752, 694, 662, 555, 486, 431 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{20}H_{14}N$ $[M]^+$ 268.1121, found 268.1112.

2,2'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate (77aPF$_6$)



According to **Procedure 5**, a solution of 0.045 g (0.071 mmol) of 2,2'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate and 0.024 g (0.149 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred over the period of 0.5 h at rt to give 2,2'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate.

Yield: 0.049 g (98%) of a yellow solid.

Mp: 226 °C.

^{1}H NMR (600 MHz, DMSO-d_6)[XV]: δ = 9.28 (d, *J* = 8.6 Hz, 2H, 4-H, 4′-H), 8.63 (d, *J* = 8,8 Hz, 2H, 8-H, 8′-H), 8.49 (d, *J* = 8.3 Hz, 2H, 3-H, 3′-H), 8.48 (d, *J* = 7.5 Hz, 2H, 5-H, 5′-H), 8.33 (t, *J* = 7,7 Hz, 2H, 7-H, 7′-H), 8.19 (s, 4H, 2′′-H, 3′′-H, 5′′-H, 6′′-H), 8.07 (t, *J* = 7.5 Hz, 2H, 6-H, 6′-H), 4.81 (s, 6H, N*C*H_3) ppm.

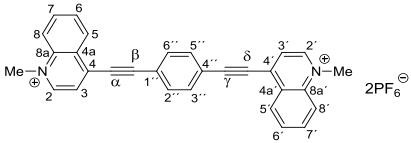
[XV] The assignment was performed according to compound with methylsulfate anion

^{13}C NMR (150 MHz, DMSO-d_6): δ = 145.7 (C4, C4′), 140.3 (C2, C2′), 139.4 (C8a, C8a′), 136.2 (C7, C7′), 133.6 (C2″, C3″, C5″, C6″), 130.4 (C5, C5′), 130.2 (C6, C6′), 128.7 (C4a, C4a′), 126.4 (C3, C3′), 122.1 (C1″, C4″), 119.6 (C8, C8′), 106.6 (Cβ, Cγ), 85.1 (Cα, Cδ), 43.0 (NCH_3, N′CH_3) ppm.

IR (ATR): 3100, 2204, 2042, 1596, 1576, 1522, 1439, 1352, 1234, 1161, 1059, 819, 602, 555, 499, 471 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0881.

4,4'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate (77bPF$_6$)



According to **Procedure 5**, a solution of 0.020 g (0.031 mmol) of 4,4'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate and 0.011 g (0.065 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred over the period of 0.5 h at rt to give 4,4'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate.

Yield: 0.021 g (99%) of a green solid.

Mp: 341°C (decomp.).

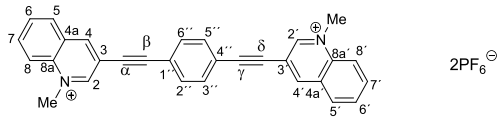
^{1}H NMR (600 MHz, DMSO-d_6)[XVI]: δ = 9.52 (d, *J* = 6.0 Hz, 2H, 2-H, 2-H′), 8.80 (d, *J* = 8.3 Hz, 2H, 5-H, 5′-H), 8.57 (d, *J* = 8.8 Hz, 2H, 8-H, 8′-H), 8.40 (d, *J* = 6.0 Hz, 2H, 3-H, 3′-H), 8.35 (t, *J* = 7.8 Hz, 2H, 7-H, 7′-H), 8.16 (t, *J* = 7.5 Hz, 2H, 6-H, 6′-H), 8.12 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 4.64 (s, 6H, NCH_3, N′CH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 149.5 (C2, C2′), 138.4 (C8a, C8a′), 137.8 (C4, C4′), 135.8 (C7, C7′), 133.4 (C2″, C3″, C5″, C6″), 130.9 (C6, C6′), 128.3 (C5, C5′), 127.9 (C4a, C4a′), 124.6 (C3, C3′), 122.5 (C1″, C4″), 119.8 (C8a, C8a′), 105.6 (Cβ, Cγ), 86.6 (Cα, Cδ), 45.5 (N*C*H$_3$, N′*C*H$_3$) ppm.

IR (ATR): 3327, 3102, 2209, 2167, 1619, 1604, 1574, 1530, 1508, 1436, 1403, 1373, 1335, 1326, 1237, 1204, 1179, 1155, 1116, 1105, 1019, 998, 828, 767, 712, 644, 556, 488, 437, 410 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0886.

3,3'-(Benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate (77cPF_6)



According to **Procedure 5**, a solution of 0.020 g (0.031 mmol) of 3,3'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dimethylsulfate and 0.011 g (0.065 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred over the period of 0.5 h at rt to give 3,3'-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate.

[XVI] The assignment was performed according to compound with methylsulfate anion

Yield: 0.021 g (99%) of yellow solid.

Mp: 224 °C.

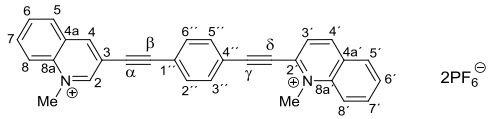
^{1}H NMR (600 MHz, DMSO-d_6)[XVII]: δ = 9.89 (d, *J* = 1.0 Hz, 2H, 2-H, 2′-H), 9.53 (s, 2H, 4-H, 4′-H), 8.55 (d, *J* = 8.9 Hz, 2H, 8-H, 8′-H), 8.47 (d, *J* = 7.5 Hz, 2H, 5-H, 5′-H), 8.33 (ddd, *J* = 1.6, 7.1, 8.7 Hz, 2H, 7-H, 7′-H), 8.11 (t, *J* = 7.9 Hz, 2H, 6-H, 6′-H), 7.83 (s, 4H, 2″-H, 3″-H, 5″-H, 6″-H), 4.67 (s, 6H, NCH_3, N′CH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (C2, C2′), 148.2 (C4, C4′), 137.4 (C8a, C8a′), 136.3 (C7, C7′), 132.3 (C2″, C3″, C5″, C6″), 130.7 (C6, C6′), 128.7 (C4a, C4a′), 122.1 (C1″, C4″), 119.3 (C8, C8′), 116.4 (C3, C3′), 93.9 (Cβ, Cγ), 85.8 (Cα, Cδ), 45.5 (N*C*H$_3$, N′*C*H$_3$) ppm.

IR (ATR): 3095, 2230, 1607, 1581, 1521, 1435, 1378, 1359, 1318, 1222, 1117, 926, 823, 767, 622, 555, 494, 483, 433 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0882.

1-Methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)quinolinium dihexafluorophosphate (77dPF$_6$)



According to **Procedure 5**, a solution of 0.020 g (0.031 mmol) of 1-methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)quinolinium dimethylsulfate and 0.011 g (0.065 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred over the period

[XVII] The assignment was performed according to compound with methylsulfate anion

of 0.5 h under rt to give 1-methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)-quinolinium dihexafluorophosphate.

Yield: 0.021 g (99%) of a yellow solid.

Mp: 217°C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[XVIII]: δ = 9.91 (d, *J* = 0.9 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.26 (d, *J* = 8.6 Hz, 1H, 4′-H), 8.62 (d, *J* = 8.9 Hz, 1H, 8′-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.48-8.46 (m, 3H, 5-H, 3′-H, 5′-H), 8.36-8.31 (m, 2H, 7-H, 7′-H), 8.14-8.11 (m, 3H, 6-H, 3″-H, 5″-H), 8.07 (t, *J* = 7.6 Hz, 1H, 6′-H), 7.91 (d, *J* = 8.4 Hz, 2H, 2″-H, 6″-H), 4.80 (s, 3H, N′CH_3), 4.67 (s, 3H, NCH_3) ppm.

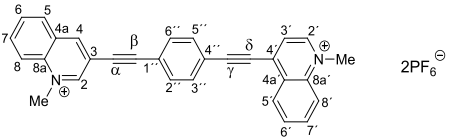
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (C2), 148.3 (C4), 145.6 (C4′), 140.2 (C2′), 139.4 (C8a′), 137.5 (C8a), 136.4 (C7), 136.2 (C7′), 133.6 (C3″, C5″), 132.4 (C2″, C6″), 130.7 (C6), 130.44 (C5 or C5′), 130.37 (C5 or C5′), 130.2 (C6′), 128.7 (C4a), 128.6 (C4a′), 126.3 (C3′), 124.1 (C1′), 120.1 (C4′), 119.6 (C8′), 119.3 (C8), 116.2 (C3), 107.1 (Cγ), 93.6 (Cβ), 86.8 (Cα), 84.6 (Cδ), 45.5 (NCH$_3$), 42.9 (N′CH$_3$) ppm.

IR (ATR): 3329, 3095, 2205, 1617, 1594, 1577, 1521, 1436, 1379, 1354, 1308, 1233, 1221, 1174, 1156, 1138, 1016, 974, 927, 819, 767, 752, 553, 498, 479, 436, 428 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0884.

[XVIII] The assignment was performed according to compound with methylsulfate anion

1-Methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl))quinolinium dihexafluorophosphate (77ePF$_6$)



According to procedure **Procedure 5**, a solution of 0.020 g (0.031 mmol) of 1-methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl))quinolinium dimethylsulfate and 0.011 g (0.065 mmol) of NH_4PF_6 in 4 mL of water mixture was stirred over the period of 0.5 h at rt to give 1-methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl))quinolinium dihexafluorophosphate.

Yield: 0.021 g (99%) of a yellow solid.

Mp: 229 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[XIX]: δ = 9.91 (d, *J* = 1.0 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.53 (d, *J* = 6.4 Hz, 1H, 2′-H), 8.81 (d, *J* = 9.0 Hz, 1H, 5′-H), 8.58 (d, *J* = 9.0 Hz, 1H, 8′-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.47 (d, *J* = 7.8 Hz, 1H, 5-H), 8.37-8.32 (m, 2H, 7-H, 7′-H), 8.17 (t, *J* = 7.5 Hz, 1H, 6′-H), 8.12 (t, *J* = 7.5 Hz, 1H, 6-H), 8.09 (d, *J* = 8.3 Hz, 2H, 3″-H, 5″-H), 7.89 (d, *J* = 8.3 Hz, 2H, 2″-H, 6″-H), 4.67 (s, 3H, NC*H*$_3$), 4.64 (s, 3H, N′C*H*$_3$) ppm.

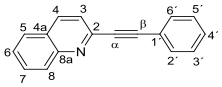
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.2 (C2), 149.5 (C2′), 148.3 (C4), 138.4 (C8a′), 138.0 (C4′), 137.5 (C8a), 136.3 (C7), 135.8 (C7′), 133.4 (C3″, C5″), 132.3 (C2″, C6″), 130.9 (C6′), 130.7 (C6), 130.4 (C5), 128.7 (C4a), 128.4 (C4a′), 127.9 (C5′), 124.4 (C3′), 123.3 (C1″), 121.3 (C4″), 119.9 (C8′), 119.3 (C8), 116.3 (C3), 105.8 (Cγ), 93.8 (Cβ), 86.4 (Cα), 86.2 (Cδ), 45.5 (N*C*H$_3$), 45.4 (N′*C*H$_3$) ppm.

[XIX] The assignment was performed according to compound with methylsulfate anion

IR (ATR): 3317, 3096, 2203, 1617, 1603, 1568, 1530, 1521, 1434, 1404, 1374, 1321, 1237, 1222, 1202, 1178, 1105, 1016, 995, 927, 821, 763, 739, 709, 644, 623, 554, 498, 488, 465, 425 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{30}H_{22}N_2$ $[M]^{2+}$ 205.0884, found 205.0890.

2-(Phenylethynyl)quinoline (79a)



According to **Procedure 1**, a solution of 0.491 g (3.00 mmol) of 2-chloroquinoline, 0.042 g (0.06 mmol) of $Pd(PPh_3)_2Cl_2$, 0.012 g (0.06 mmol) CuI and 0.367 g (3.6 mmol) of ethynylbenzene in 20 mL of anhydrous NEt_3 was heated over the period of 2 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 5:1) gave 2-(phenylethynyl)quinoline **79a**.

Yield: 0.653 g (95%) of a yellow solid.

Mp: 75 °C (72-75 °C[98]).

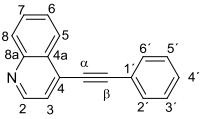
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.3 Hz, 1H, 4-H), 8.03-8.01 (m, 2H, 5-H, 8-H), 7.82 (ddd, *J* = 1.5, 6.7, 8.5 Hz, 1H, 7-H), 7.74 (d, *J* = 8.3 Hz, 1H, 3-H), 7.70-7.68 (m, 2H, 2′-H, 6′-H), 7.66 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H, 6-H), 7.53-7.48 (m, 3H, 3′-H, 4′-H, 5′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.7 (o, C8a), 142.6 (o, C2), 136.7 (+, C4), 131.9 (+, C2′, C6′), 129.7 (+, C4′), 128.9 (+, C3′, C5′), 128.6 (+, C5), 128.0 (+, C8), 127.4 (+, C6), 126.9 (o, C4a), 124.3 (+, C3), 121.2 (o, C1′), 89.5 (o, Cα), 89.1 (o, Cβ) ppm.

IR (ATR): 3053, 2208, 2161, 1616, 1591, 1552, 1498, 1441, 1425, 1310, 1295, 1211, 1142, 1115, 1070, 989, 829, 788, 769, 760, 693, 620, 548, 526, 478 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{17}H_{12}N$ $[M+H]^+$ 230.0965, found 230.0969; *m/z* calcd for $C_{17}H_{11}NNa$ $[M+Na]^+$ 252.0789, found 252.0789.

4-(Phenylethynyl)quinoline (79b)[XX]



According to **Procedure 1**, a solution of 0.624 g (3.00 mmol) of 4-bromoquinoline, 0.042 g (0.06 mmol) of $Pd(PPh_3)_2Cl_2$, 0.012 g (0.06 mmol) CuI and 0.367 g (3.6 mmol) of ethynylbenzene in 20 mL of anhydrous NEt_3 was heated over the period of 2 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 5:1) gave 4-(phenylethynyl)quinoline **79b**.

Yield: 0.674 g (98%) of yellow solid.

Mp: 45 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 4.4 Hz, 1H, 2-H), 8.38 (ddd, *J* = 0.6, 1.4, 8.3 Hz, 1H, 5-H), 8.14 (d, *J* = 8.1 Hz, 1H, 8-H), 7.76 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, 7-H), 7.68-7.66 (m, 2H, 2′-H, 6′-H), 7.64 (ddd, *J* = 1.4, 6.9, 8.2 Hz, 1H, 6-H), 7.57 (d, *J* = 4.4 Hz, 1H, 3-H), 7.44-7.42 (m, 3H, 3′-H, 4′-H, 5′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.9 (+, C2), 148.3 (o, C8a), 132.1 (+, C2′, C6′), 130.0 (+, C7, C8), 129.9 (o, C4), 129.5 (+, C4′), 128.7 (+, C3′, C5′), 127.9 (o, C4a),

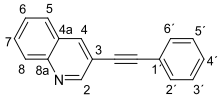
[XX] Compound was synthetized before but melting point, IR, 2D NMR and HRMS spectra were not reported

127.3 (+, C6), 126.1 (+, C5), 123.7 (+, C3), 122.4 (o, C1′), 98.8 (o, Cβ), 85.2 (o, Cα) ppm.

IR (ATR): 3085, 3051, 3029, 2998, 2212, 1961, 1919, 1595, 1576, 1505, 1487, 1441, 1418, 1390, 1363, 1310, 1277, 1217, 1192, 1175, 1134, 1068, 1029, 919, 871, 846, 815, 756, 687, 641, 579, 550, 529, 506, 485, 442 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{17}H_{12}N$ $[M+H]^+$ 230.0965, found 230.0965.

3-(Phenylethynyl)quinoline (79c)



According to **Procedure 1**, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) CuI and 1.071 g (10.50 mmol) of ethynylbenzene in 30 mL of anhydrous NEt_3 was heated over the period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(phenyl-ethynyl)quinoline **79c**[XXI].

Yield: 2.290 g (100%) of a white solid.

Mp: 83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 2.0 Hz, 1H, 2-H), 8.30 (d, *J* = 2.0 Hz, 1H, 4-H), 8.10 (d, *J* = 8.3 Hz, 1H, 8-H), 7.79 (d, *J* = 8.3 Hz, 1H, 5-H), 7.72 (ddd, *J* = 1.5, 6.9, 8.3 Hz, 1H, 7-H), 7.63-7.53 (m, 3H, 6-H, 2′-H, 6′-H), 7.42-7.35 (m, 3H, 3′-H, 4′-H, 5′-H) ppm.

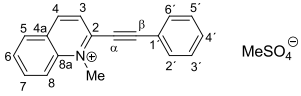
[XXI] Spectroscopic data are in agreement with those reported in the literature[99]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1 (+, C2), 146.8 (o, C8a), 138.3 (+, C4), 131.8 (+, C2′, C6′), 130.1 (+, C7), 129.4 (+, C8), 128.9 (+, C4′), 128.5 (+, C3′, C5′), 127.6 (+, C6), 127.3 (+, C5), 127.3 (o, C4a), 122.6 (o, C1′), 117.5 (o, C3), 92.7 (o, Cβ), 86.7 (o, Cα) ppm.

IR (ATR): 3008, 2162, 1619, 1599, 1564, 1484, 1443, 1409, 1368, 1294, 1196, 1124, 1113, 1072, 980, 905, 860, 784, 756, 691, 656, 640, 539, 515, 498, 474, 429 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{17}H_{11}NNa$ $[M+Na]^+$ 252.0789, found 252.0796.

1-Methyl-2-(phenylethynyl)quinolinium methylsulfate (80a)



According to **Procedure 3**, a solution of 0.057 g (0.25 mmol) of 2-(phenylethynyl)quinoline, 1 drop of nitrobenzene and 0.06 mL (0.625 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated over the period of 3 h under reflux temperature to give 1-methyl-2-(phenylethynyl)quinolinium methylsulfate **80a**.

Yield: 0.085 g (96%) of a yellow solid.

Mp: 120 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.23 (d, *J* = 8.6 Hz, 1H, 4-H), 8.59 (d, *J* = 8.9 Hz, 1H, 8-H), 8.46 (d, *J* = 7.8 Hz, 1H, 5-H), 8.43 (d, *J* = 8.6 Hz, 1H, 3-H), 8.32-8.29 (m, 1H, 7-H), 8.05 (t, *J* = 7.5 Hz, 1H, 6-H), 7.97-7.95 (m, 2H, 2′-H, 6′-H), 7.71-7.68 (m, 1H, 4′-H), 7.64-7.61 (m, 2H, 3′-H, 5′-H), 4.78 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

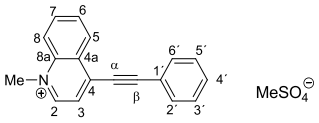
^{13}C NMR (150 MHz, DMSO-d_6): δ = 145.4 (+, C4), 140.8 (o, C2), 139.3 (o, C8a), 136.0 (+, C7), 133.1 (+, C2′, C6′), 132.4 (+, C4′), 130.3 (+, C5), 130.0 (+, C6), 129.3 (+,

C3′, C5′), 128.4 (o, C4a), 126.2 (+, C3), 119.5 (+, C8), 118.8 (o, C1′), 108.6 (o, Cβ), 82.7 (o, Cα), 52.8 (+, CH_3SO_4), 42.8 (+, NCH_3) ppm.

IR (ATR): 3531, 3474, 3062, 3016, 2980, 2941, 2199, 1618, 1601, 1576, 1520, 1441, 1359, 1311, 1243, 1221, 1155, 1060, 1003, 875, 844, 774, 745, 687, 611, 577, 542, 501, 426 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N$ $[M]^+$ 244.1126, found 244.1131.

1-Methyl-4-(phenylethynyl)quinolinium methylsulfate (80b)



According to **Procedure 3**, a solution 0.057 g (0.25 mmol) of 4-(phenylethynyl)quinoline, 1 drop of nitrobenzene and 0.06 mL (0.625 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated over the period of 1.5 h under reflux temperature to give 1-methyl-4-(phenylethynyl)quinolinium methylsulfate **80b**.

Yield: 0.088 g (100%) of a yellow solid.

Mp: 165 °C.

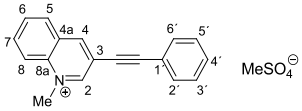
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.49 (d, *J* = 6.4 Hz, 1H, 2-H), 8.77 (d, *J* = 8.2 Hz, 1H, 5-H), 8.55 (d, *J* = 8.8 Hz, 1H, 8-H), 8.36 (d, *J* = 6.0 Hz, 1H, 3-H), 8.34 (ddd, *J* = 1.3, 7.1, 8.7 Hz, 1H, 7-H), 8.17-8.14 (m, 1H, 6-H), 7.92-7.91 (m, 2H, 2′-H, 6′-H), 7.66-7.64 (m, 1H, 4′-H), 7.61-7.58 (m, 2H, 3′-H, 5′-H), 4.63 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 149.4 (+, C2), 138.5 (o, C4), 138.4 (o, C8a), 135.7 (+, C7), 132.8 (+, C2′, C6′), 131.5 (+, C4′), 130.8 (+, C6), 129.2 (+, C3′, C5′), 128.4 (o, C4a), 127.9 (+, C5), 124.2 (+, C3), 119.9 (o, C1′), 119.8 (+, C8), 107.3 (o, Cβ), 84.1 (o, Cα), 52.8 (+, CH_3SO_4), 45.3 (+, NCH_3) ppm.

IR (ATR): 3022, 2944, 2199, 1605, 1575, 1529, 1496, 1441, 1400, 1374, 1325, 1224, 1059, 1012, 840, 766, 731, 691, 608, 575, 546, 533, 503, 469, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N$ $[M]^+$ 244.1126, found 244.1117.

1-Methyl-3-(phenylethynyl)quinolinium methylsulfate (80c)



According to **Procedure 3**, a solution of 1.145 g (5.00 mmol) of 3-(phenylethynyl)quinoline, 1 drop of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated over the period of 1.5 h under reflux temperature to give 1-methyl-3-(phenylethynyl)quinolinium methylsulfate **80c**[XXII].

Yield: 1.686 g (95%) of a yellow solid.

Mp: 224 °C (decomp.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.87 (s, 1H, 2-H), 9.50 (s, 1H, 4-H), 8.54 (d, *J* = 8.8 Hz, 1H, 8-H), 8.45 (d, *J* = 8.8 Hz, 1H, 5-H), 8.31 (ddd, *J* = 1.3, 7.1, 8.8 Hz, 1H, 7-H), 8.10 (t, *J* = 8.8 Hz, 1H, 6-H), 7.74-7.66 (m, 2H, 2′-H, 6′-H), 7.60-7.50 (m, 3H, 3′-H, 4′-H, 5′-H), 4.66 (s, 3H, NCH_3), 3.38 (s, 3H, CH_3SO_4) ppm.

[XXII] Spectroscopic data are in agreement with those reported in the literature[64]

^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.1 (+, C2), 147.9 (+, C4), 137.3 (o, C8a), 136.0 (+, C7), 131.7 (+, C2′, C6′), 130.6 (+, C4′), 130.3 (+, C6), 130.2 (+, C5), 129.1 (+, C3′, C5′), 128.7 (o, C4a), 120.5 (o, C1′), 119.2 (+, C8), 116.7 (o, C3), 94.8 (o, Cβ), 83.3 (o, Cα), 52.8 (+, CH_3SO_4), 45.4 (+, NCH_3) ppm.

IR (ATR): 3043, 2941, 2223, 1631, 1606, 1578, 1520, 1493, 1494, 1444, 1365, 1227, 1210, 1173, 1140, 1059, 1010, 929, 910, 878, 766, 737, 695, 607, 577, 552, 524, 501, 479, 429 cm^{-1}.

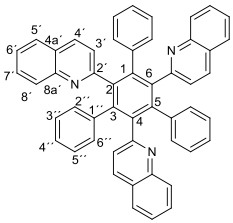
MS (ESI): *m/z* = 244.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N$ $[M]^+$ 244.1121, found 244.1126.

General procedure for the synthesis on substituted benzenes (Procedure 6)

2-(Phenylethynyl)quinoline (0.21 g, 0.92 mmol) was dissolved in anhydrous dioxane (4 mL) in an oven dried Schlenk flask under a nitrogen atmosphere and the flask was evacuated and filled with nitrogen repeatedly (3 ×). Then, $Co_2(CO)_8$ (0.015 g) was added to the flask under a nitrogen atmosphere and the flask was evacuated and filled with nitrogen again (3 ×). The resulting mixture was refluxed for 14 h and dioxane was evaporated. The resulting residue was dissolved in dichloromethane and filtered through a short pad of silica gel. Evaporation of the solvent afforded a dark colored solid which was purified by column chromatography with PE - EE as an eluent.

1,3,5-Triphenyl-2,4,6-tri(quinoline-2-yl)benzene (85)



Yield: 0.021 g (10%) of a white solid.

Mp: 337 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.83 (d, J = 8.5 Hz, 3H, 4′-H), 7.72 (d, J = 8.5 Hz, 3H, 8′-H), 7.67 (d, J = 7.9 Hz, 3H, 5′-H), 7.57 (t, J = 7.3 Hz, 3H, 7′-H), 7.41 (t, J = 7.3 Hz, 3H, 6′-H), 7.22 (d, J = 8.5 Hz, 3H, 3′-H), 7.05 (br s, 6H, 2″-H, 6″-H), 6.70 (br s, 6H, 3″-H, 5″-H), 6.63 (t, J = 7.3 Hz, 3H, 4″-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 158.9 (o, C2′), 146.4 (o, 8a′), 139.9 (o, C2, C4; C6), 139.8 (o, C1, C3, C5), 138.7 (o, C1″), 134.1 (+, C4′), 130.6[XXIII] (+,C2″, C6″) 129.0 (+, C7′), 128.6 (+, C8′), 127.4 (+, C5′), 126.3 (+, C3″, C5″), 126.1 (+, C6′), 125.8 (+, C4″), 125.4 (o, C4a′), 124.2 (+, C3′) ppm.

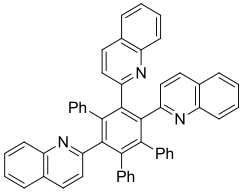
IR (ATR): 3058, 3038, 3007, 1617, 1595, 1557, 1501, 1443, 1424, 1332, 1305, 1253, 1223, 1156, 1139, 1113, 1073, 1031, 959, 906, 838, 753, 698, 619, 587, 515, 476, 431, 423, 412 cm^{-1}.

MS (ESI): m/z = 688.5 $[M+H]^+$.

HRMS (ESI): m/z calcd for $C_{51}H_{34}N_3$ $[M+H]^+$ 688.2745, found 688.2743.

[XXIII] This ^{13}C signal is not a singlet-like, it is broad signal almost not visible in spectrum ^{13}C, additionally recognized by HSQC spectrum

1,2,4-Triphenyl-3,5,6-tri(quinoline-2-yl)benzene (86)



Yield: 0.063 g (30%) of a white solid.

Mp: 318 °C.

^{1}H NMR (600 MHz, DMSO-d_6)[XXIV]: δ = 7.85 (d, *J* = 7.5 Hz, 1H), 7.76-7.68 (m, 4H), 7.57-7.53 (m, 5H), 7.45-7.42 (m, 3H), 7.32-7.29 (m, 2H), 7.22-7,20 (m, 3H), 7.04-6.99 (m, 6H), 6.83-6.67 (m, 9H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 159.1 (o), 159.0 (o), 158.8 (o), 146.4 (o), 146.3 (o), 146.2 (o), 140.5 (o), 140.4 (o), 140.2 (o), 139.8 (o), 139.6 (o), 139.3 (o), 139.0 (o), 138.9 (o), 138.6 (o), 134.1 (+), 133.6 (+), 130.8 (+), 130.3 (br, +), 129.0 (+), 128.8 (+), 128.6 (+), 128.3 (+), 127.4 (+), 127.3 (+), 126.6 (+), 126.5 (+), 126.1 (+), 125.92 (+), 125.85 (+), 125.81 (+), 125.7 (+), 125.3 (o), 125.2 (o), 124.3 (+), 124.2 (+) ppm.

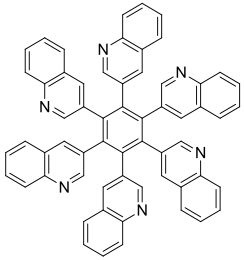
IR (ATR): 3056, 3023, 1737, 1597, 1559, 1501, 1441, 1424, 1294, 1160, 1142, 1294, 1160, 1142, 1111, 1072, 1029, 942, 849, 835, 818, 751, 722, 699, 606, 531, 514, 479, 423, 417 cm^{-1}.

MS (ESI): *m/z* = 688.3 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{51}H_{34}N_3$ $[M+H]^+$ 688.2745, found 688.2739.

[XXIV] All substituents are not equivalent, but with similar chemical shifts, because using 2D spectra are not helpful for assignment of atom signals

***Hexakis*(quinoline-3-yl)benzene (97)**



Hexakis(quinoline-3-yl)benzene was prepared by an identical procedure (**Procedure 6**) using *bis*(quinoline-3-yl)acetylene (0.295 g, 0.35 mmol) as above. A dark colored solid was purified by column chromatography with EE, then MeOH - $CHCl_3$ (1 : 3) as eluents.

Yield: 0.295 g (85%) of a white solid.

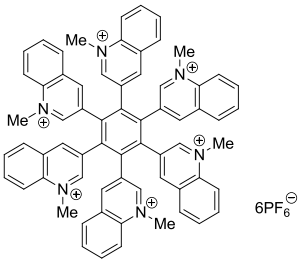
Mp: >370 °C.

The compound is insoluble in all NMR solvents which we tested.

IR (ATR): 3025, 1619, 1602, 1567, 1489, 1355, 1317, 1260, 1195, 1126, 1110, 1043, 1017, 974, 953, 905, 858, 785, 744, 696, 605, 527, 474, 439 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{60}H_{36}N_6Na$ $[M+Na]^+$ 863.2899, found 863.2896.

***Hexakis*(1-methylquinolinium-3-yl)benzene *hexakis* hexafluorophosphate (88)**



According to **Procedure 3**, a solution of 0.084 g (0.10 mmol) of *hexakis*(quinoline-3-yl)benzene, 1 drop of nitrobenzene and 0.10 mL (1.00 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature. Then the obtained salt was dissolved in water and precipitated with 1.05 equiv of NH_4PF_6 to give *hexakis*(1-methylquinolinium-3-yl)benzene *hexakis* hexafluorophosphate **88**.

Yield: 0.171 g (95%) of a white solid.

Mp: 195 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.41-8.89 (m, 12H), 8.34-8.16 (m, 18H), 8.00-7.92 (m, 6H), 4.44-4.28 (m, 18H) ppm.

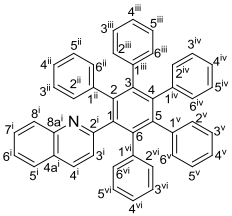
^{13}C NMR (150 MHz, DMSO-d_6): δ = 148.7, 148.2, 137.9, 137.8, 137.7, 137.5, 137.0, 131.0, 130.4, 128.6, 128.0, 119.4, 45.97, 45.89, 45.85, 45.79 ppm.

IR (ATR): 3084, 1631, 1582, 1524, 1451, 1382, 1228, 1173, 1040, 952, 920, 827, 771, 753, 740, 614, 556, 494, 440, 413 cm^{-1}.

General procedure of preparation of propeller-like compounds (Procedure 7)

Benzophenone (10 g) was melted in a 50 mL round-bottomed flask fitted with an air condenser. Corresponding phenylethynylquinoline (2.00 mmol) and tetraphenylcyclopentadienone (2.50 mmol) were added to the flask, which was heated for 0.5 h using a heat gun. The solution was cooled to rt and toluene (10 mL) was added to prevent the solidification of the benzophenone. After cooling, *n*-hexane (50 mL) was added, resulting in the precipitation of a product, which was collected by vacuum filtration.

2,3,4,5,6-Pentaphenyl-1-(quinoline-2-yl)benzene (81a)



2,3,4,5,6-Phenyl-1-(quinoline-2-yl)benzene **81a** was prepared by **Procedure 7** using 2-(phenylethynyl)quinoline (0.158 g, 0.690 mmol) and tetraphenylcyclopentadienone (0.394 g, 1.035 mmol) in benzophenone (5 g) in 10 mL round-bottomed flask in 0.75 h.

Yield: 0.260 g (64%) of a white solid.

Mp: >360 °C.

^{1}H NMR (600 MHz, $CDCl_3$)[XXV]: δ = 7.75 (d, *J* = 8.6 Hz, 1H, 8^i-H), 7.64 (d, *J* = 8.5 Hz, 1H, 4^i-H), 7.55 (dd, *J* = 1.2, 8.2 Hz, 1H, 5^i-H), 7.51 (ddd, *J* = 1.5, 6.9, 8.5 Hz, 1H, 7^i-H), 7.36 (ddd, *J* = 1.1, 7.0, 8.1 Hz, 1H, 6^i-H), 7.01 (d, *J* = 8.5 Hz, 1H, 3^i-H), 7.00-6.96 (m,

[XXV] All signals which are marked as "Ph" are belong to molecule (phenyl rest) but not possible to assign

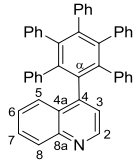
2H, Ph), 6.93-6.83 (m, 16 H, 2^{ii}-H, 6^{ii}-H, 2^{iii}-H, 6^{iii}-H, 2^{v}-H, 6^{v}-H, 2^{vi}-H, 6^{vi}-H, 3^{ii}-H, 5^{ii}-H, 3^{iii}-H, 5^{iii}-H, 3^{v}-H, 5^{v}-H, 3^{vi}-H, 5^{vi}-H), 6.79-6.72 (m, 7H, Ph) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.2 (o, $C2^{i}$), 147.1 (o, $C8a^{i}$), 141.6 (o, $C1^{iv}$), 140.8/140.4/140.3/140.1 (o, C2, C3, C5, C6, $C1^{ii}$, $C1^{iii}$, $C1^{v}$, $C1^{vi}$), 140.6 (o, C4), 140.0 (o, C1), 134.2 (+, $C4^{i}$), 131.7/131.5/131.4/130.7 (+, Ph), 129.05 (+, $C7^{i}$), 129.00 (+, $C8^{i}$), 127.3 (+, $C5^{i}$), 126.8 (+, Ph), 126.0 (+, $C6^{i}$), 125.7 (o, $C4a^{i}$), 125.51/125.45 (+, Ph) ppm.

IR (ATR): 3055, 3025, 1597, 1558, 1501, 1441, 1403, 1323, 1300, 1221, 1154, 1073, 1029, 948, 839, 812, 753, 718, 695, 617, 583, 555, 531, 478 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{45}H_{32}N$ $[M+H]^+$ 586.2530, found 586.2531.

2,3,4,5,6-Pentaphenyl-1-(quinoline-4-yl)benzene (81b)



2,3,4,5,6-Pentaphenyl-1-(quinoline-4-yl)benzene **81b** was prepared by **Procedure 7** using 4-(phenylethynyl)quinoline (0.302 g, 1.319 mmol) and tetraphenylcyclopentadienone (0.430 g, 1.121 mmol, 0.85 equiv) in benzophenone (10 g) in 50 mL round-bottomed flask in 0.5 h (total conversion of dienone).

Yield: 0.529 g (81%) of a white solid.

Mp: 323 °C.

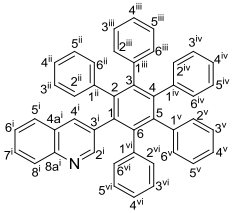
^{1}H NMR (600 MHz, $CDCl_3$)[XXVI]: δ = 8.49 (d, *J* = 4.4 Hz, 1H, 2-H), 7.86 (dd, *J* = 0.5, 7.9 Hz, 1H, 5-H), 7.80 (d, *J* = 8.3, 1H, 8-H), 7.50 (ddd, *J* = 1.5, 6.9, 8.4 Hz, 1H, 7-H), 7.39 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1H, 6-H), 7.05 (d, *J* = 4.4 Hz, 1H, 3-H), 6.93-6.82 (m, 17H, Ph), 6.77-6.75 (m, 2H, Ph), 6.68-6.64 (m, 4H, Ph), 6.55-6.52 (m, 2H, Ph) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.8 (+, C2), 147.9 (o, C4), 147.7 (o, C8a), 141.5 (o), 140.74 (o), 140.70 (o), 140.4 (o), 140.2 (o), 139.7 (o), 136.0 (o, Cα), 131.53 (+), 131.46 (+), 131.44 (+), 130.9 (+), 130.2 (+), 129.3 (+, C8), 128.8 (+, C7), 128.0 (o, C4a), 127.2 (+, C5), 126.84 (+), 126.81 (+), 126.7 (+), 126.6 (+), 125.8 (+), 125.7 (+, C6), 125.5 (+), 124.4 (+, C3) ppm.

IR (ATR): 3052, 3025, 1598, 1496, 1440, 1385, 1291, 1071, 1028, 905, 852, 817, 759, 736, 718, 695, 616, 586, 562, 551, 542, 463, 449, 425 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{45}H_{32}N$ $[M+H]^+$ 586.2530, found 586.2522.

2,3,4,5,6-Pentaphenyl-1-(quinoline-3-yl)benzene (81c)



2,3,4,5,6-Pentaphenyl-1-(quinoline-3-yl)benzene **81c** was prepared by **Procedure 7** using 3-(phenylethynyl)quinoline (0.458 g, 2.00 mmol) and tetraphenylcyclopentadienone (0.961 g, 2.50 mmol) in benzophenone (10 g) in 50 mL round-bottomed flask in 0.5 h.

[XXVI] All signals which are marked as "Ph" are belong to molecule (phenyl rest) but not possible to assign

Yield: 0.590 g (51%) of a white solid.

Mp: 334 °C.

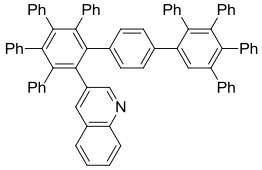
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 2 Hz, 1H, 2^{i}-H), 7.84 (d, *J* = 8.4 Hz, 1H, 8^{i}-H), 7.59 (d, *J* = 2 Hz, 1H, 4^{i}-H), 7.53-7.51 (m, 1H, 7^{i}-H), 7.43 (d, *J* = 8.0 Hz, 5^{i}-H), 7.35-7.33 (m, 1H, 6^{i}-H), 6.88-6.85 (m, 20H, 2^{ii}-H, 6^{ii}-H, 2^{iii}-H, 6^{iii}-H, 2^{iv}-H, 6^{iv}-H, 2^{v}-H, 6^{v}-H, 2^{vi}-H, 6^{vi}-H, 3^{ii}-H, 5^{ii}-H, 3^{iii}-H, 5^{iii}-H, 3^{iv}-H, 5^{iv}-H, 3^{v}-H, 5^{v}-H, 3^{vi}-H, 5^{vi}-H), 6.83-6.78 (m, 4H, 4^{ii}-H, 4^{iii}-H, 4^{v}-H, 4^{vi}-H), 6.78-6.77 (m, 1H, 4^{iv}-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.9 (+, $C2^{i}$), 145.6 (o, $C8a^{i}$), 141.4 (o, C4), 141.07 (o, C2, C6), 140.88 (o, C3, C5), 140.44 (o, $C1^{iv}$), 140.34 (o, $C1^{ii}$, $C1^{vi}$), 139.96 (o, $C1^{iii}$, $C1^{v}$), 137.8 (+, $C4^{i}$), 136.51 (o, C1), 134.2 (o, $C3^{i}$), 131.51/131.48/131.45/131.41/131.37 (+, $C2^{ii}$, $C6^{ii}$, $C2^{iii}$, $C6^{iii}$, $C2^{iv}$, $C6^{iv}$, $C2^{v}$, $C6^{v}$, $C2^{vi}$, $C6^{vi}$), 129.0 (+, $C8^{i}$), 128.9 (+, $C7^{i}$), 127.6 (+, $C5^{i}$), 127.4/127.0/126.85/126.83/126.78 (+, $C3^{ii}$, $C5^{ii}$, $C3^{iii}$, $C5^{iii}$, $C3^{iv}$, $C5^{iv}$, $C3^{v}$, $C5^{v}$, $C3^{vi}$, $C5^{vi}$),127.1 (o, $C4a^{i}$), 126.2 (+, $C6^{i}$), 125.87 (+, $C4^{ii}$, $C4^{vi}$), 125.54 (+, $C4^{iii}$, $C4^{v}$), 125.52 (+, $C4^{iv}$) ppm.

IR (ATR): 3055, 3024, 1662, 1600, 1495, 1440, 1401, 1354, 1311, 1275, 1261, 1127, 1070, 1029, 966, 906, 838, 817, 779, 747, 738, 719, 695, 647, 638, 555, 544, 535, 480, 443, 413 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{45}H_{32}N$ $[M+H]^+$ 586.2529, found 586.2530.

1-(Quinolin-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)-benzene (81d)



1-(Quinolin-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene **81d** was prepared by **Procedure 7** using 3-((4-ethynylphenyl)ethynyl)quinoline (0.290 g, 1.146 mmol) and tetraphenylcyclopentadienone (1.320 g, 3.438 mmol, 3.0 equiv) in benzophenone (10 g) in 50 mL round-bottomed flask in 0.5 h.

Yield: 0.885 g (77%) of a brown solid.

Mp: 368 °C (decomp.).

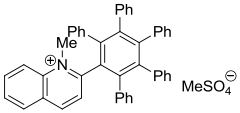
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.57 (ddd, *J* = 1.4, 6.8, 8.3 Hz, 1H), 7.55 (d, J = 2H, 1H), 7.46-7.45 (m, 1H), 7.41-7.38 (m, 1H), 7.23 (s, 1H), 7.15-1.13 (m, 2H), 7.07-7.06 (m, 2H), 6.94-6.55 (m, 40H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.9 (+), 145.7 (o), 141.8 (o), 141.7 (o), 141.3 (o), 141.1 (o), 140.86 (o), 140.82 (o), 140.80 (o), 140.73 (o), 140.48 (o), 140.43 (o), 140.34 (o), 140.27 (o), 140.21 (o), 140.07 (o), 139.95 (o), 139.7 (o), 139.3 (o), 139.1 (o), 138.8 (o), 137.9 (o), 137.8 (+), 136.5 (o), 134.2 (o), 132.5 (+), 131.6 (+), 131.5 (+), 131.39 (+), 131.35 (+), 131.0 (+), 130.9 (+), 130.2 (+), 130.0 (+), 129.1 (+), 128.89 (+), 128.87 (+), 128.77 (+), 128.4 (+), 127.69 (+), 127.62 (+), 127.3 (+), 127.1 (+), 127.0 (+), 126.96 (o), 126.82 (+), 126.76 (+), 126.66 (+), 126.31 (+), 126.2 (+), 125.8 (+), 125.64 (+), 125.55 (+), 125.50 (+), 125.46 (+), 125.36 (+) ppm.

IR (ATR): 3024, 1599, 1490, 1441, 1398, 1275, 1071, 1021, 907, 851, 763, 696, 638, 615, 566, 554, 480, 425 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{75}H_{51}NNa$ $[M+Na]^+$ 988.3914, found 988.3901.

2,3,4,5,6-Pentaphenyl-1-(1-methylquinolinium-2-yl)benzene methylsulfate (82a)



According to **Procedure 3**, a solution of 0.100 g (0.171 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-2-yl)benzene, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 2,3,4,5,6-pentaphenyl-1-(1-methylquinolinium-2-yl)benzene methylsulfate **82a**.

Yield: 0.115 g (95%) of a white solid.

Mp: 190 °C.

^{1}H NMR (600 MHz, DMSO-d_6)[XXVII]: δ = 8.88 (d, *J* = 8.5 Hz, 1H, 4^i-H), 8.31 (d, *J* = 9.0 Hz, 1H, 8^i-H), 8.24-8.23 (m, 2H, 3^i-H, 5^i-H), 8.14 (t, *J* = 8.0 Hz, 7^i-H), 7.93 (t, *J* = 7.4 Hz, 6^i-H), 7.10-6.84 (m, 25H, Ph), 4.41 (s, 3H, $N^iC\mathit{H_3}$), 3.38 (s, 3H, $C\mathit{H_3}SO_4$) ppm.

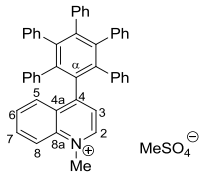
^{13}C NMR (150 MHz, DMSO-d_6): δ = 159.1 (o, $C2^i$), 144.2 (+, $C4^i$), 143.9 (o, C1), 141.2 (o), 139.1 (o), 138.9 (o), 138.3 (o), 137.5 (o, $C8a^i$), 137.4 (o), 136.0 (+, $C7^i$), 131.7 (+), 130.9 (+), 130.6 (+), 130.4 (+), 130.4 (+, $C6^i$), 130.3 (+, $C5^i$), 130.26 (+), 130.0 (+), 129.3 (+), 126.7 (+), 127.43 (o, $C4a^i$), 127.39 (+, $C3^i$), 127.2 (+), 126.95 (+), 126.91 (+), 126.86 (+), 126.2 (+), 126.0 (+), 119.1 (+, $C8^i$), 52.8 (+, $C\mathit{H_3}SO_4$), 42.5 (+, $N^iC\mathit{H_3}$) ppm.

[XXVII] All signals which are marked as "Ph" are belong to molecule (phenyl rest) but not possible to assign

IR (ATR): 3056, 3023, 1619, 1600, 1577, 1519, 1497, 1442, 1409, 1347, 1252, 1224, 1176, 1152, 1073, 1059, 1013, 918, 849, 817, 770, 756, 723, 698, 644, 608, 576, 554, 532, 428 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{46}H_{34}N$ $[M]^+$ 600.2686, found 600.2692.

2,3,4,5,6-Pentaphenyl-1-(1-methylquinolinium-4-yl)benzene methylsulfate (82b)



According to **Procedure 3**, a solution of 0.154 g (0.263 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-4-yl)benzene, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 2,3,4,5,6-pentaphenyl-1-(1-methylquinolinium-4-yl)benzene methylsulfate **82b**.

Yield: 0.185 g (99%) of a brownish solid.

Mp: 355 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[XXVIII]: δ = 9.14 (d, *J* = 6.0 Hz, 1H, 2-H), 8.27 (dd, *J* = 1.0, 8.4 Hz, 1H, 5-H), 8.20 (d, *J* = 8.9 Hz, 1H, 8-H), 8.15 (d, *J* = 6.0 Hz, 1H, 3-H), 8.11 (ddd, *J* = 1.4, 7.1, 8.7 Hz, 1H, 7-H), 7.96-7.94 (m, 1H, 6-H), 7.06 (d, *J* = 7.7 Hz, 2H, Ph), 7.01 (d, *J* = 7.7 Hz, 2H, Ph), 6.95-6.83 (m, 14H, Ph), 6.74-6.71 (m, 4H, Ph), 6.60-6.57 (m, 2H, Ph), 4.42 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

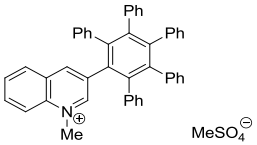
[XXVIII] All signals which are marked as "Ph" are belong to molecule (phenyl rest) but not possible to assign

^{13}C NMR (150 MHz, DMSO-d_6): δ = 158.5 (o, C4), 147.5 (+, C2), 142.3 (o), 140.6 (o), 139.36 (o), 139.34 (o), 138.9 (o), 138.3 (o), 137.1 (o, C8a), 135.2 (+, C7), 133.1 (o, Cα), 131.0 (+), 130.8 (+), 130.52 (+), 130.49 (+), 129.8 (+, C6), 129.3 (+, C5), 128.3 (o, C4a), 126.83 (+), 126.78 (+), 126.74 (+), 126.71 (+), 126.67 (+), 126.4 (+), 125.81 (+), 125.77 (+), 125.3 (+, C3), 118.8 (+, C8), 52.8 (+, *C*H$_3$SO$_4$), 45.0 (+, N*C*H$_3$) ppm.

IR (ATR): 3051, 3025, 1622, 1615, 1599, 1586, 1577, 1531, 1495, 1441, 1401, 1389, 1375, 1335, 1265, 1216, 1118, 1059, 1015, 869, 820, 766, 726, 695, 609, 576, 553, 542, 464, 430 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{46}H_{34}N$ $[M]^+$ 600.2686, found 600.2673.

2,3,4,5,6-Phenyl-1-(1-methylquinolinium-3-yl)benzene methylsulfate (82c)



According to **Procedure 3**, a solution of 0.100 g (0.171 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-3-yl)benzene, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 2,3,4,5,6-phenyl-1-(1-methylquinolinium-3-yl)benzene methylsulfate **92c**.

Yield: 0.122 g (99%) of a light green solid.

Mp: 321 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.35 (d, *J* = 1.4 Hz, 1H, 2-H), 8.84 (s, 1H, 4-H), 8.24 (d, *J* = 8.1 Hz, 1H, 8-H), 8.14 (ddd, *J* = 1.5, 7.1, 8.8 Hz, 1H, 7-H), 8.06 (dd, *J* = 1.1,

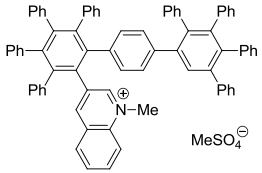
8.4 Hz, 1H, 5-H), 7.92-7.90 (m, 1H, 6-H), 7.05 (d, *J* = 7.7 Hz, 2H, Ph), 7.02 (d, *J* = 7.7 Hz, 2H, Ph), 6.96-6.82 (m, 21H, Ph), 4.34 (s, 3H, NC*H*$_3$), 3.37 (s, 3H, C*H*$_3$SO$_4$) ppm.

^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ = 150.6 (+, C2), 147.5 (+, C4), 142.3 (o), 140.7 (o), 140.5 (o), 139.3 (o), 139.0 (o), 138.4 (o), 135.53 (o, C8a), 135.48 (+, C7), 134.4 (o, C3), 132.8 (o, C1′), 131.0 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.54 (+), 130.5 (+, C6), 129.9 (+, C5), 127.7 (o, C4a), 127.4 (o), 126.89 (+), 126.87 (+), 126.80 (+), 126.77 (+), 126.4 (+), 125.92 (+), 125.85 (+), 118.9 (+, C8), 52.8 (+, *C*H$_3$SO$_4$), 44.8 (+, NCH$_3$) ppm.

IR (ATR): 3051, 3023, 2961, 1600, 1524, 1496, 1442, 1378, 1254, 1215, 1063, 1012, 760, 697, 618, 577, 558, 441 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{46}H_{34}N$ $[M]^+$ 600.2686, found 600.2687.

1-(1-Methylquinolinium-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)-phenyl)benzene methylsulfate (82d)



According to **Procedure 3**, a solution of 0.481 g (0.5 mmol) of 1-(quinolin-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-(1-methylquinolinium-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene methylsulfate.

Yield: 0.521 g (96%) of a khaki solid.

Mp: 222 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[XXIX]: δ = 9.28 (d, *J* = 1.3 Hz, 1H, Q), 8.73 (s, 1H, Q), 8.35 (d, *J* = 6.7 Hz, 1H, Q), 8.20 (ddd. *J* = 1.6, 7.0, 8.7 Hz, 1H, Q), 8.05-8.04 (m, 1H, Q), 7.98-7.95 (m, 1H, Q), 7.26-7.23 (m, 1H, Ph), 7.19-7.13 (m, 4H, Ph), 7.02-6.99 (m, 3H, Ph), 6.95-6.74 (m, 28H, Ph), 6.71-6.64 (m, 5H, Ph), 6.61-6.53 (m, 3H, Ph), 6.49-6.47 (m, 1H, Ph), 4.33 (s, 3H, NCH_3), 3.36 (s, 3H, CH_3SO$_4$) ppm.

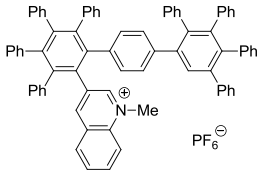
^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.6 (+), 147.5 (+), 142.2 (o), 141.5 (o), 140.9 (o), 140.7 (o), 140.6 (o), 140.4 (o), 140.3 (o), 140.0 (o), 139.6 (o), 139.3 (o), 139.01 (o), 139.00 (o), 138.96 (o), 138.8 (o), 138.6 (o), 138.4 (o), 137.3 (o), 136.5 (o), 135.6 (o), 135.5 (+), 134.4 (o), 132.8 (o), 131.0 (+), 130.9 (+), 130.8 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.55 (+), 130.53 (+), 130.44 (+), 130.36 (+), 130.28 (+), 130.0 (+), 129.4 (+), 128.9 (+), 128.6 (+), 128.4 (+), 128.2 (+), 127.73 (+), 127.66 (+), 127.4 (+), 126.85 (+), 126.81 (+), 126.51 (+), 126.46 (+), 126.4 (+), 125.91 (+), 125.85 (+), 125.8 (+), 125.44 (+), 125.37 (+), 125.31 (+), 118.9 (+), 52.7 (+), 44.8 (+) ppm.

IR (ATR): 3055, 3023, 1600, 1524, 1442, 1378, 1249, 1222, 1178, 1157, 1138, 1058, 1008, 911, 852, 797, 766, 697, 565, 496, 432 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{76}H_{54}N$ $[M]^+$ 980.4251, found 980.4257.

[XXIX] All signals which are marked as “Ph” or “Q” are belong phenyl rests or quinolinium ring

1-(1-Methylquinolinium-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene hexafluorophosphate (82dPF$_6$)



A suspension of 0.050 g (0.046 mmol) of 1-(1-methylquinolinium-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene methylsulfate and 0.008 g (0.049 mmol) of NH_4PF_6 in 4 mL of water was stirred for 1 day at rt to give 1-(1-methylquinolinium-3-yl)-2,3,4,5,-tetraphenyl-6-(4-(1,2,3,4-tetraphenyl)phenyl)benzene hexafluorophosphate **82dPF$_6$**.

Yield: 0.049 g (95%) of a yellow solid.

Mp: 220 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6)[xxx]: δ = 9.28 (s, 1H, Q), 8.73 (s, 1H, Q), 8.35 (d, *J* = 8.9 Hz, 1H, Q), 8.20 (t, J = 7.7 Hz, 1H, Q), 8.05 (d, *J* = 7.9 Hz, 1H, Q), 7.96 (t, *J* = 7.5 Hz, 1H, Q), 7.26 (m, 1H, Ph), 7.17-7.14 (m, 4H, Ph), 7.02-6.47 (m, 40H, Ph), 4.33 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.6 (+), 147.5 (+), 142.2 (o), 141.5 (o), 140.9 (o), 140.7 (o), 140.6 (o), 140.4 (o), 140.3 (o), 140.0 (o), 139.6 (o), 139.3 (o), 139.01 (o), 139.00 (o), 138.96 (o), 138.8 (o), 138.6 (o), 138.4 (o), 137.3 (o), 136.5 (o), 135.6 (o), 135.5 (+), 134.4 (o), 132.8 (o), 131.0 (+), 130.9 (+), 130.8 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.55 (+), 130.53 (+), 130.44 (+), 130.36 (+), 130.28 (+), 130.0 (+), 129.4 (+), 128.9 (+), 128.6 (+), 128.4 (+), 128.2 (+), 127.73 (+), 127.66 (+), 127.4 (+), 126.85

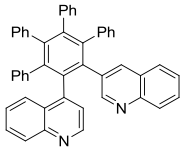
[xxx] All signals which are marked as “Ph” or “Q” are belong phenyl rests or quinolinium ring

(+), 126.81 (+), 126.51 (+), 126.46 (+), 126.4 (+), 125.91 (+), 125.85 (+), 125.8 (+), 125.44 (+), 125.37 (+), 125.31 (+), 118.9 (+), 44.8 (+) ppm.

IR (ATR): 3055, 3027, 1600, 1521, 1495, 1442, 1379, 1072, 1028, 835, 766, 697, 557, 427 cm^{-1}.

HRMS (ESI): *m/z* calcd for for $C_{76}H_{54}N$ $[M]^+$ 980.4251, found 980.4238.

1-(Quinoline-3-yl)-2-(quinoline-4-yl)-3,4,5,6-tetraphenylbenzene (83a)



1-(Quinoline-3-yl)-2-(quinoline-4-yl)-3,4,5,6-tetraphenylbenzene **83a** was prepared by **Procedure 7** using 4-(quinolin-3-ylethynyl)quinoline (0.264 g, 0.943 mmol) and tetraphenylcyclopentadienone (0.543 g, 1.414 mmol) in benzophenone (5 g) in 10 mL round-bottomed flask in 0.5 h. The solution was cooled to rt and benzene (4 mL) was added to prevent the solidification of the benzophenone. Then solvents were evaporated with silica gel and obtained solid was purified by column chromatography with EE/PE (1:1) as eluents to give **83a**.

Yield: 0.0659 g (11%) of a white solid.

Mp: 300 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6, 25 °C)[XXXI]: δ = 8.58 (d, *J* = 2.2 Hz, 1H), 8.46-8.44 (m, 2H), 8.25 (d, *J* = 2.2 Hz, 1H), 7.97-7.96 (m, 1H), 7.91-7.87 (m, 2H), 7.61-7.49 (m, 10H),

[XXXI] Compound **83a** exists in two rotameric forms (~ 1:1) with close chemical shifts and exact description is not possible

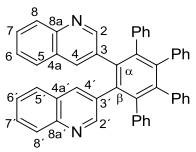
7.47 (ddd, *J* = 1.6, 6.8, 8.4 Hz, 2H), 7.45 (ddd, *J* = 1.5, 6.6, 8.2 Hz, 1H), 7.41-7.39 (m, 2H), 7.36 (ddd, *J* = 1.2, 6.8, 8.1 Hz, 1H), 7.26-7.24 (m, 1H), 7.21-7.19 (m, 1H), 7.13-7.00 (m, 8H), 6.96-6.81 (m, 22H), 6.79-6.72 (m, 3H), 6.71-6.67 (m, 4H), 6.55 (t, *J* = 7.6 Hz, 2H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6, 25 °C): δ = 151.50 (+), 150.81 (+), 148.76 (+), 148.58 (+), 146.85 (o), 146.78 (o) ,145.98 (o), 145.89 (o), 145.00 (o), 144.90 (o), 141.21 (o), 141.18 (o), 141.07 (o), 141.01 (o), 140.86 (o), 140.70 (o), 140.29 (o), 140.20 (o), 139.52 (o), 139.45 (o), 139.17 (o), 139.15 (o), 139.05 (o), 138.94 (o), 136.72 (+), 136.35 (o), 136.29 (o), 135.89 (o), 135.82 (o), 135.61 (+), 132.66 (o), 132.55 (o), 131.11 (+), 130.98 (+), 130.94 (+), 130.90 (+), 130.81 (+), 130.76 (+), 130.71 (+), 130.63 (+), 130.60 (+), 130.58 (+), 130.53 (+), 130.42 (+), 129.36 (+), 129.07 (+), 129.01 (+), 128.95 (+), 128.75 (+), 128.68 (+), 128.21 (+), 127.63 (+), 127.31 (+), 126.93 (+), 126.89 (+), 126.81 (+), 126.76 (+), 126.72 (+), 126.67 (+), 126.63 (+), 126.49 (+), 126.45 (+), 126.40 (+), 126.33 (+), 126.24 (+), 125.89 (+), 125.83 (+), 125.73 (+), 125.65 (+), 124.37 (+), 123.82 (+) ppm.

IR (ATR): 3055, 3027, 1699, 1600, 1585, 1567, 1505, 1490, 1463, 1442, 1384, 1359, 1126, 1072, 1027, 965, 908, 854, 814, 761, 696, 617, 533, 480 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{48}H_{33}N_2$ $[M+H]^+$ 637.2639, found 637.2629.

1,2-Di(quinoline-3-yl)-3,4,5,6-tetraphenylbenzene (83b)



According to **Procedure 7,** benzophenone (5 g) was melted in a 50 mL round-bottomed flask fitted with an air condenser. 3,3'-Ethyne-1,2-diyldiquinoline (0.280 g, 1.00 mmol)

and tetraphenylcyclopentadienone (0.576 g, 1.50 mmol) were added to the flask, which was heated for 1 h using an open flame. The solution was cooled to rt and benzene (3 mL) was added to prevent the solidification of the benzophenone. After cooling, *n*-hexane (200 mL) was added, resulting in the precipitation of 1,2-di(quinoline-3-yl)-3,4,5,6-tetraphenylbenzene **83b** as a white powder, which was washed with *n*-hexane and toluene, and collected by vacuum filtration.

Yield: 0.570 g (90%) of a white solid.

Mp: 344 °C.

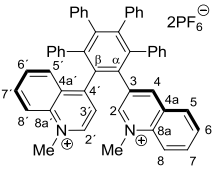
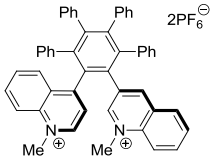
^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.52 (d, *J* = 2.1 Hz, 2H, 2-H, 2′-H), 7.97 (d, *J* = 1.7 Hz, 1H, 4-H), 7.93 (d, *J* = 1.7 Hz, 1H, 4′-H), 7.64-7.61 (m, 2H, 8-H, 8′-H), 7.59 (d, *J* = 7.9 Hz, 1H, 5-H), 7.52 (d, *J* = 8.3 Hz, 1H, 5′-H), 7.50-7.47 (m, 2H, 7-H, 7′-H), 7.38-7.36 (m, 1H, 6-H), 7.35-7.32 (m, 1H, 6′-H), 7.01-6.74 (m, 20H, Ph) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.0 (+, C2), 151.8 (+, C2′), 144.99 (o, C8a′), 144.98 (o, C8), 141.06 (o), 141.04 (o), 140.9 (o), 139.5 (o), 139.29 (o), 139.25 (o), 137.4 (+, C4′), 137.0 (+, C4), 136.95 (o, Cα), 136.93 (o, Cβ), 132.97 (o), 132.94 (o), 130.93 (+), 130.89(+), 130.77 (+), 130.72 (+), 130.70 (+), 129,66 (+), 129.51 (+), 129.18 (+, C7 or C7′), 129.16 (+, C7 or C7′), 128.34 (+, C8 or C8′), 128.31 (+, C8 or C8′), 127.8 (+, C5), 127.6 (+, C5′), 127.0 (+), 126.8 (+), 126.7 (+), 126.5 (+, C6, C6′), 126.3 (o, C4a or C4a′), 126.20 (o, C4a or C4a′), 125.9 (+), 125.7 (+) ppm.

IR (ATR): 3055, 3025, 1600, 1552, 1490, 1401, 1314, 1241, 1127, 1071, 966, 907, 812, 784, 747, 696, 632, 536, 476 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{48}H_{33}N_2$ $[M+H]^+$ 637.2639, found 637.2637.

1-(1-Methylquinolinium-3-yl)-2-(1-methylquinolinium -4-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate (84a)

84a*   **84a#**

A solution of 0.050 g (0.079 mmol) of 1-(quinoline-3-yl)-2-(quinoline-4-yl)-3,4,5,6-tetraphenylbenzene, 1 drop of nitrobenzene and 0.02 mL (0.21 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature, cooled to rt and extracted with water (3 × 5 mL) and then precipitated with excess of NH_4PF_6 (1.3 equiv) to give 1-(1-methylquinolinium-3-yl)-2-(1-methylquinolinium-4-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate **84a**.

Yield: 0.067 g (89%) of a yellow solid.

Mp: 245 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6, 25 °C)[XXXII]: δ = 9.54# (d, *J* = 1.3 Hz, 1H, 2-H), 9.23* (d, *J* = 1.5 Hz, 1H, 2-H), 9.20# (d, *J* = 6.3 Hz, 1H, 2′-H), 9.18* (d, *J* = 6.4 Hz, 1H, 2′-H), 9.02* (d, *J* = 1.5 Hz, 1H, 4-H), 8.81# (s, 1H, 4-H), 8.34# (dd, *J* = 1.1, 8.6 Hz, 1H), 8.26-8.20 (m, 6H), 8.16# (d, *J* = 6.3 Hz, 1H, 3′-H), 8.15-8.07 (m, 7H), 8.04-8.01# (m, 2H), 7.92* (ddd, *J* = 1.2, 6.8, 8.1 Hz, 1H), 7.85-7.79# (m, 2H), 7.21-6.62*# (m, 40H, Ph), 4.37# (s, 3H, N′CH_3), 4.346# (s, 3H, NCH_3), 4.343* (s, 3H, N′CH_3), 4.10* (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6, 25 °C): δ = 155.64*/# (o, C4′), 155.59*/# (o, C4′), 149.53# (+, C2), 149.31* (+, C2), 148.47# (+, C2′), 148.42* (+, C2′), 147.14* (+, C4), 146.81# (+, C4), 142.92 (o), 142.90 (o), 142.89 (o), 142.84 (o), 141.63 (o), 141.49 (o),

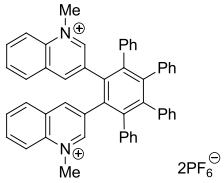
[XXXII] Compound **84a** exists in two rotameric forms (**84a***: **84a#** ~ 1 : 1.27) with close chemical shifts and exact description is not possible

140.37 (o), 140.21 (o), 138.56 (o), 138.48 (o), 138.35 (o), 138.31 (o), 137.54 (o), 137.52 (o), 137.48 (o), 137.43 (o), 136.38[#] (o, C8a), 136.10* (o, C8a), 135.96 (+), 135.88 (+), 135.46 (+), 135.38 (+), 133.36* (o, Cβ), 133.23[#] (o, Cβ), 132.26 (o), 132.21 (o), 132.05 (o), 131.97 (o), 131.16 (+), 130.88 (+), 130.73 (+), 130.63 (+), 130.61 (+), 130.58 (+), 130.55 (+), 130.51 (+), 130.42 (+), 130.30 (+), 130.26 (+), 130.23 (+), 130.22 (+), 129.71 (+), 129.63 (+), 129.50 (+), 128.60 (+), 128.32 (+), 127.88 (o), 127.71 (o), 127.61 (+), 127.59 (+), 127.44 (+), 127.37 (+), 127.15 (+), 127.07 (+), 127.03 (+), 126.98 (+), 126.93 (+), 126.85 (+), 126.79 (+), 126.64 (+), 126.30 (+), 126.26 (+), 126.24 (+), 125.24 (+), 124.78 (+), 119.34 (+), 119.02 (+), 118.86 (+), 45.37 (+), 45.33 (+), 45.30 (+), 44.67* (+, N*C*H$_3$) ppm.

IR (ATR): 3057, 1619, 1605, 1588, 1529, 1498, 1443, 1234, 1175, 1115, 1073, 1025, 1001, 918, 827, 765, 702, 619, 556, 492, 434 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{50}H_{38}N_2$ $[M]^{2+}$ 333.1512, found 333.1512.

1,2-Di(1-methylquinolinium-3-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate (84b)



A solution of 0.050 g (0.079 mmol) of 1,2-di(quinoline-3-yl)-3,4,5,6-tetraphenylbenzene, 1 drop of nitrobenzene and 0.02 mL (0.21 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature, cooled to rt and extracted with water (3 × 5 mL) and precipitated with excess of NH_4PF_6

(1.3 equiv) to give 1,2-di(1-methylquinolinium-3-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate **84b**.

Yield: 0.068 g (90%) of a white solid.

Mp: 240 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.43 (d, *J* = 1.3 Hz, 1H, 2-H), 9.40 (d, *J* = 1.3Hz, 1H, 2′-H), 9.05 (s, 1H, 4′-H), 8.88 (s, 1H, 4-H), 8.30 (d, *J* = 8.8 Hz, 1H, 8-H or 8′-H), 8.27 (d, *J* = 8.9 Hz, 1H, 8-H or 8′-H), 8.16-8.09 (m, 4H, 5-H, 5′-H, 7-H, 7′-H), 7.93-7.90 (m, 2H, 6-H, 6′-H), 7.05-6.84 (m, 20H, Ph), 4.38 (s, 3H, N′CH_3), 4.32 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.6 (+, C2), 149.8 (+, C2′), 147.9 (+, C4′), 147.6 (+, C4), 142.8 (o), 142.7 (o), 141.9 (o), 141.8 (o), 138.5 (o), 137.6 (o), 136.5 (o, C8a′), 136.4 (o, C8a), 135.94 (+, C7 or C7′), 135.85 (+, C7 or C7′), 133.10 (o, Cβ), 132.99 (o, Cα), 132.4 (o), 132.2 (o), 130.89 (+)[XXXIII], 130.75 (+), 130.69 (+), 130.60 (+), 130.48 (+), 130.44 (+), 130.42 (+), 130.38 (+), 130.33 (+), 130.31 (+), 130.22 (+, C5), 130.07 (+, C5′), 127.92 (o, C4a or C4a′), 127.89 (o, C4a or C4a′), 127.6 (+), 127.0 (+), 126.7 (+), 126.3 (+), 119.00 (+, C8 or C8′), 118.90 (+, C8 or C8′), 45.4 (+, N′CH$_3$), 45.2 (+, NCH$_3$) ppm.

IR (ATR): 3057, 3027, 1631, 1602, 1583, 1523, 1497, 1443, 1380, 1356, 1334, 1230, 1174, 1141, 1115, 1073, 1024, 936, 830, 769, 744, 702, 619, 556, 524, 504, 419 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{50}H_{38}N_2$ $[M]^{2+}$ 333.1512, found 333.1518.

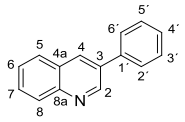
[XXXIII] Some of signals with value 130 ppm belong to C6 and C6′

5.4 Experiments to chapter 3.3.1 – 3.3.2

General procedure for the preparation of the 3-arylquinolines (Procedure 8; Suzuki-Miyaura coupling)

Under a nitrogen atmosphere, 1.040 g (5.00 mmol) of 3-bromoquinoline were dissolved in 20 mL of anhydrous toluene and treated with 10 mol-% of $Pd(CH_3COO)_2$ The mixtures were then subjected to ultrasound irradiation for 5 min and then stirred at rt for additional 0.5 h. Then 6.00 mmol of the boronic acid, 40.00 mmol of potassium phosphate and 4 mL of water were added, and the mixtures were heated under reflux for 24 h. The mixtures were then allowed to cool to rt, treated with dichloromethane (50 mL) and washed with water. The organic phases were then dried over $MgSO_4$ and filtered, and the solvents were removed *in vacuo*. The resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.

3-Phenylquinoline (89a)



According to **Procedure 8**, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline, 0.112 g (0.50 mmol) of $Pd(CH_3COO)_2$, 0.732 g (6.00 mmol) phenylboronic acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-phenylquinoline **89a**.

Yield: 0.820 g (80%) of a brownish solid.

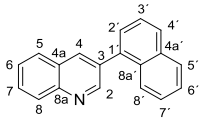
Mp: 50 °C.

^{1}H NMR (600 MHz, $CDCl_3$)[XXXIV]: δ = 9.20 (s, 1H, 2-H), 8.31 (d, *J* = 1.8 Hz, 1H, 4-H), 8.16 (d, *J* = 8.3 Hz, 1H, 8-H), 7.89 (d, *J* = 8.1 Hz, 1H, 5-H), 7.74–7.71 (m, 3H, 7-H, 2′-H, 6′-H), 7.58 (t, *J* = 7.4 Hz, 1H, 6-H), 7.54–7.52 (m, 2H, 3′-H, 5′-H), 7.44 (m, 1H, 4′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.0 (+, C2), 147.4 (o, C8a), 138.0 (o, C1′), 134.0 (o, C3), 133.4 (+, C4), 129.5 (+, C7), 129.3 (o, C4a), 129.3 (+, C8, C3′, C5′), 128.3 (+, C4′), 128.2 (+, C5), 127.6 (+, C2′, C6′), 127.2 (+, C6) ppm.

IR (ATR): 3027, 1568, 1492, 1368, 1340, 1027, 952, 914, 861, 785, 773, 762, 693, 624, 612, 560, 545, 494, 479, 443 cm^{-1}.

3-(Naphthalen-1-yl)quinoline (89b)



According to **Procedure 8**, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline, 0.112 g (0.50 mmol) of $Pd(CH_3COO)_2$, 1.032 g (6.00 mmol) naphthalene-1-boronic acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(naphthalen-1-yl)quinoline **89b**.

Yield: 1.071 g (84%) of a white solid.

Mp: 57 °C.

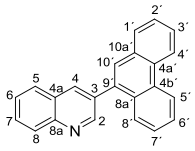
[XXXIV] This spectrum is in agreement with previously reported spectral data[100]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.08 (d, *J* = 1.9 Hz, 1H, 2-H), 8.28 (d, *J* = 1.9 Hz, 1H, 4-H), 8.23 (d, *J* = 8.5 Hz, 1H, 8-H), 7.97 (m, 1H, 5′-H), 7.95 (m, 1H, 4′-H), 7.90 (d, *J* = 7.9 Hz, 1H, 5-H), 7.87 (d, *J* = 8.5 Hz, 1H, 8′-H) 7.79 (ddd, *J* = 1.4, 7.0, 8.4 Hz, 1H, 7-H), 7.63 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H, 6-H), 7.60 (dd, *J* = 7.0, 8.2 Hz, 1H, 3′-H), 7.54 (ddd, *J* = 1.2, 6.7, 8.0 Hz, 1H, 6′-H), 7.53 (dd, *J* = 1.2, 7.0 Hz, 1H, 2′-H), 7.47 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, 7′-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.0 (+, C2), 147.4 (o. C8a), 136.5 (+, C4), 136.4 (o, C1′), 134.0 (o, C4a′), 133.9 (o, C3), 131.8 (o, C8a′), 129.8 (+, C7), 129.4 (+, C8), 128.8 (+, C4′), 128.7 (+, C5′), 128.1 (+, C5), 128.0 (o, C4a), 127.9 (+, C2′), 127.2 (+, C6), 126.8 (+, C7′), 126.3 (+, C6′), 125.6 (+, C3′), 125.5 (+, C8′) ppm.

IR (ATR): 3034, 1811, 1566, 1508, 1490, 1396, 1364, 1332, 1125, 1017, 941, 904, 861, 774, 745, 664, 616, 566, 479, 450, 430 cm^{-1}.

3-(Phenanthren-9-yl)quinoline (89c)



According to **Procedure 8**, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline, 0.112 g (0.50 mmol) of $Pd(CH_3COO)_2$, 1.332 g (6.00 mmol) phenanthrene-9-boronic acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(phenanthren-9-yl)quinoline **89c**.

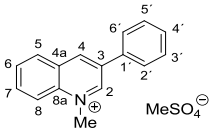
Yield: 1.068 g (70%) of a light-yellow oil[XXXV].

^{1}H NMR (400 MHz, $CDCl_3$)[XXXVI]: δ = 9.12-9.11 (m, 1H), 8.82-8.80 (m, 1H), 8.76-8.74 (m, 1H), 8.32-8.31 (m, 1H), 8.24-8.23 (m, 1H), 7.94-7.89 (m, 2H), 7.88-7.86 (m, 1H), 7.81-7.79 (m, 1H), 7.78-7.77 (m, 1H), 7.72-7.69 (m, 2H), 7.66-7.61 (m, 2H), 7.57-7.54 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 147.6, 136.4, 135.1, 133.9, 132.4, 131.0, 130.9, 130.4, 129.8, 129.5, 128.9, 128.9, 128.1, 128.0, 127.3, 127.2, 127.2, 127.0, 127.0, 126.5, 123.3, 122.8 ppm.

IR (ATR): 3058, 1732, 1618, 1566, 1489, 1449, 1337, 1239, 1123, 1044, 914, 891, 861, 787, 743, 723, 616, 537, 511, 479, 427, 411 cm^{-1}.

1-Methyl-3-phenylquinolinium methylsulfate (90a)



According to **Procedure 3**, a solution of 0.513 g (2.50 mmol) of 3-phenylquinoline, 1 drop of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in 15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-phenylquinolinium methylsulfate **90a**.

Yield: 0.796 g (96%) of a yellow solid.

Mp: 211 °C.

[XXXV] Even after long time under high vacuum compound stay oil
[XXXVI] This spectrum is in agreement with previously reported spectral data[101]

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.96 (d, *J* = 1.4 Hz, 1H, 2-H), 9.62 (d, *J* = 1.4 Hz, 1H, 4-H), 8.53 (d, *J* = 8.9 Hz, 1H, 8-H), 8.49 (d, *J* = 8.9 Hz, 1H, 5-H), 8.27 (ddd, *J* = 1.5, 7.1, 8.9 Hz, 1H, 7-H), 8.08 (ddd, *J* = 1.5, 7.1, 8.9 Hz, 1H, 6-H), 8.04–8.03 (m, 2H, 2′-H, 6′-H), 7.66 (t, 2H, *J* = 7.62 Hz, 3′-H, 5′-H), 7.60–7.58 (m, 1H, 4′-H), 4.72 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO_4) ppm.

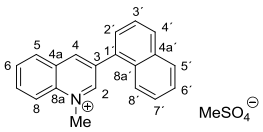
^{13}C NMR (150 MHz, DMSO-d_6): δ = 149.3 (+, C2), 142.9 (+, C4), 137.2 (o, C8a), 135.2 (+, C7), 133.5 (o, C3), 133.4 (o, C1′), 130.5 (+, C5), 130.2 (+, C6), 129.8 (+, C4′), 129.5 (+, C3′, C5′), 129.2 (o, C4a), 127.4 (+, C2′, C6′), 119.0 (+, C8), 52.8 (+, CH_3SO_4), 45.4 (+, NCH_3) ppm.

IR (ATR): 3052, 1534, 1504, 1362, 1206, 1051, 1006, 859, 773, 733, 695, 607, 576, 496, 457, 427 cm^{-1}.

MS (ESI): *m/z* = 220.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{16}H_{14}N$ [M]$^+$ 220.1121, found 220.1126.

1-Methyl-3-(naphthalen-1-yl)quinolinium methylsulfate (90b)



According to **Procedure 3**, a solution of 0.638 g (2.50 mmol) of 3-(naphthalen-1-yl)quinoline, 1 drop of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in 15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate **90b**.

Yield: 0.916 g (96%) of a yellow solid.

Mp: 219 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.82 (d, *J* = 1.3 Hz, 1H, 2-H), 9.47 (s, 1H, 4-H), 8.61 (d, *J* = 8.9 Hz, 1H, 8-H), 8.54 (d, *J* = 8.2 Hz, 1H, 5-H), 8.35 (ddd, *J* = 1.5, 7.2, 8.8 Hz, 1H, 7-H), 8.19 (t, *J* = 4.7 Hz, 1H, 3′-H), 8.15–8.12 (m, 2H, 6-H, 5′-H), 7.95 (d, *J* = 8.4 Hz, 1H, 8′-H), 7.76–7.75 (m, 2H, 2′-H, 4′-H), 7.67 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H, 6′-H), 7.62 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H, 7′-H), 4.73 (s, 1H, NC*H*$_3$), 3.36 (s, 3H, C*H*$_3$SO$_4$) ppm.

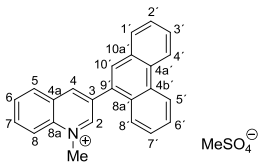
^{13}C NMR (150 MHz, DMSO-d_6): δ = 151.1 (+, C2), 146.6 (+, C4), 137.5 (o, C8a), 135.4 (+, C7), 133.4 (o, C3), 132.3 (o, C1′), 130.6 (o, C8a′), 130.5 (+, C5), 130.2 (+, C6), 129.9 (+, C3′), 129.2 (+, C4a), 128.9 (+, C4′), 128.6 (+, C5′), 127.5 (+, C7′), 126.7 (+, C6′), 125.7 (+, C2′), 124.7 (+, C8′), 119.0 (+, C8), 52.8 (+, *C*H$_3$SO$_4$), 45.3 (+, N*C*H$_3$) ppm.

IR (ATR): 3041, 2935, 2829, 1524, 1383, 1247, 1215, 1060, 1011, 807, 774, 738, 650, 609, 579, 576, 551, 483, 433 cm^{-1}.

MS (ESI): *m/z* = 270.1 [M]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N$ [M]$^+$ 270.1283, found 270.1285.

1-Methyl-3-(phenanthren-9-yl)quinolinium methylsulfate (90c)



According to **Procedure 3,** a solution of 0.638 g (2.50 mmol) of 3-(phenanthren-9-yl)quinoline, 1 drop of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in

15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate **90c**.

Yield: 1.046 g (97%) of a yellow solid.

Mp: 209 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.89 (d, *J* = 1.1 Hz, 1 H, 2-H), 9.54 (s, 1H, 4-H), 9.05 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.98 (d, *J* = 8.2 Hz, 1H, 4′-H), 8.63 (d, *J* = 9.2 Hz, 1H, 8-H), 8,56 (d, *J* = 8.2 Hz, 1H, 5-H), 8.37 (ddd, *J* = 1.5, 7.2, 8.8 Hz, 1H, 7-H), 8.16-8.11 (m, 3H, 6-H, 1′-H, 10′-H) 7.98 (d, *J* = 7.6 Hz, 1H, 8′-H), 7.86-7.83 (m, 2H, 3′-H, 6′-H), 7.78 (m, 1H, 2′-H), 7.71 (ddd, *J* = 0.9, 7.2, 8.0 Hz, 1H, 7′-H), 4.74 (s, 3H, NCH_3), 3.36 (s, 3H, CH_3SO_4) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 151.1 (+, C2), 146.7 (+, C4), 137.7 (o, C8a), 135.5 (+, C7), 133.5 (o, C3), 131.1 (o, C9′), 130.6 (o, C10a′), 130.5 (+, C5), 130.2 (+, C6), 130.2 (o, C4b′), 130.1 (o, C4a′), 130.0 (+, C10 ′), 129.5 (o, C8a′), 129.2 (o, C4a), 129.1 (+, C1′), 128.2 (+, C3′), 127.7 (+, C2′), 127.6 (+, C7′), 127.6 (+, C6′), 125.9 (+, C8′), 123.7 (+, C5), 123.1 (+, C4′), 119.0 (+, C8), 52.8 (+, *C*H_3SO_4), 45.3 (+, N*C*H_3) ppm.

IR (ATR): 3042, 2944, 1627, 1607, 1578, 1525, 1495, 1447, 1378, 1316, 1217, 1059, 1010, 900, 825, 726, 657, 608, 577, 426 cm^{-1}.

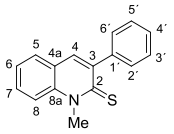
HRMS (ESI): *m/z* calcd for $C_{24}H_{18}N$ $[M]^+$ 320.1434, found 320.1435.

General procedure for the preparation of thiones (Procedure 9)

Under a nitrogen atmosphere the corresponding salt (1.00 mmol), sulfur (4.00 mmol) and LiOH (8.00 mmol) were suspended in absolute toluene (10 mL), and then potassium *tert*-pentoxide (1.20 mmol, 1.7 M solution in toluene) was added slowly with

stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. After the mixture was concentrated *in vacuo*, the crude product was purified by column chromatography with petrol ether-ethyl acetate as an eluent.

1-Methyl-3-phenylquinoline-2(1H)-thione (95a)



According to **Procedure 9**, a solution of 0.331 g (1.00 mmol) of 1-methyl-3-phenylquinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-phenylquinoline-2(1H)-thione **95a**.

Yield: 0.050 g (20%) of an orange solid.

Mp: 118 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.65 (m, 2H, 5-H, 7-H), 7.63-7.60 (m, 2H, 4-H, 8-H), 7.50-7.49 (m, 2H, 2′-H, 6′-H), 7.44-7.41 (m, 2H, 3′-H, 5′-H), 7.40-7.35 (m, 2H, 6-H, 4′-H), 4.41 (s, 3H, NCH_3) ppm.

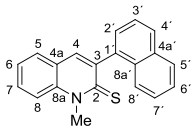
^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.0 (o, C2), 143.0 (o, C3), 141.3 (o, C8a), 140.9 (o, C1′), 132.1 (+, C4), 131.2 (+, C7), 129.6 (+, C2′, C6′), 129.1 (+, C5), 128.0 (+, C3′, C5′), 127.9 (+, C4′), 124.3 (+, C6), 123.8 (o, C4a), 115.8 (+, C8), 39.1 (+, NCH_3) ppm.

IR (ATR): 1612, 1595, 1563, 1493, 1443, 1414, 1372, 1346, 1324, 1299, 1233, 1215, 1180, 1146, 1121, 1091, 1054, 1028, 1000, 973, 964, 947, 911, 876, 852, 782, 757, 746, 740, 692, 646, 618, 595, 576, 551, 500, 481, 466, 452, 447 cm^{-1}.

MS (ESI): *m/z* = 252.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NS$ $[M+H]^+$ 252.0847, found 252.0848.

1-Methyl-3-(naphthalen-1-yl)quinoline-2(1H)-thione (95b)



According to **Procedure 9**, a solution of 0.381 g (1.00 mmol) of 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinoline-2(1H)-thione **95b**.

Yield: 0.115 g (38%) of an orange solid.

Mp: 216 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 4.6 Hz, 1H, 4′-H), 7.89 (d, *J* = 4.6 Hz, 1H, 5′-H), 7.73 (s, 1H, 4-H), 7.71-7.65 (m, 3H, 5-H, 7-H, 8-H), 7.62 (d, *J* = 8.4 Hz, 1H, 8′-H), 7.55 (m, 1H, 3′-H), 7.46 (m, 1H, 6′-H), 7.42-7.36 (m, 3H, 6-H, 2′-H, 7′-H), 4.45 (s, 3H, NCH_3) ppm.

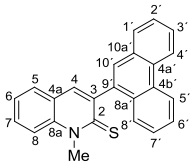
^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.4 (o, C2), 142.2 (o, C3), 141.2 (o, C8a), 139.0 (o, C1′), 133.7 (o, C4a), 133.4 (+, C4), 131.9 (o, C8a′), 131.4 (+, C7), 129.2 (+, C5), 128.6 (+, C4′), 128.4 (+, C5′), 126.8 (+, C2′), 126.2 (+, C7), 126.0 (+, C8), 125.9 (+, C6′), 125.6 (+, C3′), 124.3 (+, C6), 123.7 (o, C4a), 115.9 (+, C8), 38.9 (+, N*C*H$_3$) ppm.

IR (ATR): 1615, 1602, 1594, 1563, 1505, 1494, 1464, 1446, 1410, 1376, 1347, 1338, 1322, 1291, 1239, 1222, 1176, 1146, 1096, 1086, 1054, 1034, 1022, 1008, 970, 954, 943, 904, 879, 851, 796, 773, 761, 747, 731, 711, 664, 649, 637, 594, 581, 563, 511, 491, 474, 461, 452, 447, 425, 413 cm^{-1}.

MS (ESI): *m/z* = 302.1 [M+H]$^+$.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NS$ [M+H]$^+$ 302.1003, found 302.1003.

1-Methyl-3-(phenanthren-9-yl)quinoline-2(1H)-thione (95c)



According to **Procedure 9**, a solution of 0.431 g (1.00 mmol) of 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinoline-2(1H)-thione **95c**.

Yield: 0.316 g (90%) of an orange solid.

Mp: 227 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.73 (d, *J* = 8.3 Hz, 1H, 4′-H), 7.88 (d, *J* = 7.9 Hz, 1H, 1′-H), 7.81 (s, 1H, 4-H), 7.74-7.66 (m, 6H, 4-H, 7-H, 8-H, 3′-H, 8′-H, 10′-H), 7.63 (ddd, *J* = 1.2, 7.1, 8.2 Hz, 1H, 6′-H), 7.60 (ddd, *J* = 0.8, 7.1, 7.7 Hz, 1H, 2′-H), 7.49 (ddd, *J* = 1.1, 7.0, 8.1 Hz, 1H, 7′-H), 7.40 (ddd, *J* = 1.2, 7.0, 8.0 Hz, 1H, 6-H), 4.47 (s, 3H, NCH_3) ppm.

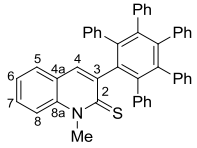
^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.3 (o, C2), 142.5 (o, C3), 141.2 (o, C8a), 137.9 (o, C9′), 133.6 (+, C4), 131.9 (o, C10a), 131.4 (+, C7), 131.1 (o, C8a′), 130.6 (o, C4a′), 130.5 (o, C4b′), 129.2 (+, C5), 128.9 (+, C1′), 127.3 (+, C10′), 127.0 (+, C8′), 126.9 (+, C3′), 126.8 (+, C2′), 126.6 (+, C7′), 126.6 (+, C6′), 124.3 (+, C6), 123.7 (o, C4a), 123.1 (+, C5), 122.8 (+, C4 ′), 115.9 (+, C8), 38.8 (+, NCH_3) ppm.

IR (ATR): 1611, 1595, 1563, 1525, 1494, 1456, 1449, 1424, 1386, 1369, 1347, 1328, 1309, 1271, 1244, 1233, 1210, 1185, 1166, 1144, 1110, 1097, 1088, 1038, 1009, 951, 945, 915, 909, 892, 874, 857, 846, 783, 759, 749, 739, 721, 701, 658, 636, 617, 611, 582, 557, 529, 506, 499, 486, 428 cm^{-1}.

MS (ESI): *m/z* = 352.1 $[M+H]^+$.

HRMS (ESI): *m/z* calcd for $C_{24}H_{18}NS$ $[M+H]^+$ 352.1160, found 352.1155.

1-Methyl-3-(4',5',6'-triphenyl-[1,1':2',1''-terphenyl]-3'-yl)quinoline-2(1H)-thione (95d)



According to **Procedure 9**, a solution of 0.154 g (0.22 mmol) of 2,3,4,5,6-phenyl-1-(1-methylquinolinium-3-yl)benzene methylsulfate, 0.055 g (1.72 mmol) of sulfur, 0.042 g

(1.82 mmol) of LiOH, potassium *tert*-pentoxide (0.26 mmol, 1.7 M solution in toluene) in 5 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(4',5',6'-triphenyl-[1,1':2',1''-terphenyl]-3'-yl)quinoline-2(1H)-thione **95d**.

Yield: 0.050 g (38%) of a yellow solid.

Mp: >330 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (ddd, *J* = 1.6, 7.1, 8.7 Hz, 1H, 7-H), 7.41 (s, 1H, 4-H), 7.39 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H), 7.37-7.36 (m, 2H, Ph), 7.30 (d, *J* = 8.6 Hz, 1H, 8-H), 7.17 (ddd, *J* = 0.7, 7.2, 8.1 Hz, 1H, 6-H), 6.93-6.76 (m, 23H, Ph), 4.00 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 184.7 (o, C2), 142.4 (o, C3), 140.8 (o), 140.65 (o), 140.61 (o), 140.5 (o), 140.03 (o), 139.99 (o, C8a), 138.8 (o), 135.3 (+, C4), 131.9 (+), 131.8 (+), 131.6 (+), 131.4 (+), 131.1 (+), 130.9 (+), 130.5 (+, C7), 128.6 (+, C5), 126.80 (+), 126.76 (+), 126.54 (+), 126.47 (+), 126.0 (+), 125.7 (+), 125.2 (+), 123.5 (+, C6), 122.9 (o, C4a), 115.4 (+, C8), 38.4 (+, NCH_3) ppm.

IR (ATR): 3055, 3022, 2922, 2850, 1733, 1616, 1568, 1495, 1441, 1372, 1315, 1235, 1184, 1148, 1095, 1072, 1043, 1027, 909, 792, 740, 695, 644, 552, 502, 481 cm^{-1}.

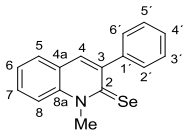
HRMS (ESI): *m/z* calcd for $C_{46}H_{33}NNaS$ $[M+Na]^+$ 654.2220, found 654.2200.

General procedure for the preparation of selenones (Procedure 10)

Under a nitrogen atmosphere, the corresponding salt (1.00 mmol), selenium (4.00 mmol) and LiOH (8.00 mmol) were suspended in absolute toluene (10 mL), then potassium *tert*-pentoxide (1.20 mmol, 1.7 M solution in toluene) was added slowly with stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. Afterward, the mixture

was concentrated *in vacuo* and the crude product was purified by column chromatography with petrol ether-ethyl acetate as eluent.

1-Methyl-3-phenylquinoline-2(1H)-selenone (96a)



According to **Procedure 10**, a solution of 0.331 g (1.00 mmol) of 1-methyl-3-phenylquinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-phenylquinoline-2(1H)-selenone **96a**.

Yield: 0.059 g (20%) of a red oil[XXXVII].

^{1}H NMR (600 MHz, $CDCl_3$ + TMS): δ = 7.74–7.69 (m, 4H, 4-H, 5-H, 7-H, 8-H), 7.47–7.37 (m, 6H, 6-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 4.56 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$ + TMS): δ = 186.4 (o, C2), 146.7 (o, C3), 142.7 (o, C1′), 141.5 (o, C8a), 131.4 (+, C7), 130.4 (+, C4), 129.7 (+, C2′, C6′), 129.3 (+, C5), 127.9 (+, C3′, C4′, C5′), 125.0 (+, C6), 125.0 (o, C4a), 116.4 (+, C8), 43.9 (+, NCH_3) ppm.

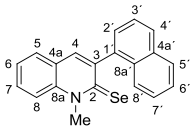
^{77}Se NMR (114 MHz, $CDCl_3$) δ = 706.6 ppm.

IR (ATR): 1639, 1591, 1559, 1493, 1443, 1371, 1321, 1234, 1142, 1070, 907, 790, 743, 694, 638, 590, 576, 480 cm^{-1}.

HRMS (APCI)[XXXVIII]**:** *m/z* calcd for $C_{16}H_{14}NSe$ $[M+H]^+$ 300.0286, found 300.0275.

[XXXVII] Not stable compound, in reaction mixture and chloroform, decompose to 3-phenylquinoline

1-Methyl-3-(naphthalen-1-yl)quinoline-2(1H)-selenone (96b)



According to **Procedure 10**, a solution of 0.381 g (1.00 mmol) of 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinoline-2(1H)-selenone **96b**.

Yield: 0.220 g (63%) of a red solid.

Mp: 196 °C (decomp.).

^{1}H NMR (600 MHz, $CDCl_3$): 7.90 (m, 2H, 4′-H, 5′-H), 7.82 (s, 1H, 4-H), 7.80 (d, *J* = 8.7 Hz, 1H, 8-H), 7.75 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7-H), 7.70 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H) 7.61 (d, *J* = 8.4 Hz, 1H, 8′-H), 7.56 (dd, *J* = 6.9, 8.2 Hz, 1H, 3′-H), 7.47-4.43 (m, 2H, 6-H, 6′-H) 7.42 (dd, *J* = 1.1, 7.0 Hz, 1H, 2′-H), 7.38 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, 7′-H), 4.59 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.8 (o, C2), 145.9 (o, C3),141.8 (o, 8a), 140.3 (o, C1′), 133.6 (o, C4a′), 132.0 (o, C8a′), 131.8 (+, C4), 131.7 (+, C7), 129.4 (+, C5), 128.5 (+, C5 ′), 128.3 (+, C4 ′), 127.0 (+, C2′), 126.1 (+, C7′), 126.0 (+, C8′), 125.9 (+, C6), 125.6 (+, C3′), 125.0 (+, C6′), 124.9 (o, C4a), 116.4 (+, C8), 43.7 (+, NCH_3) ppm.

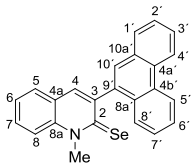
^{77}Se NMR (114 MHz, $CDCl_3$ + TMS) δ = 716.8 ppm.

IR (ATR): 3051, 3017, 2919, 2849, 2185, 1967, 1733, 1610, 1560, 1373, 1238, 1145, 1096, 1067, 795, 773, 761, 581, 491, 423 cm^{-1}.

[xxxviii] Using HRMS (ESI) measurements not give desired peaks

HRMS (APCI)[XXXIX]**:** *m/z* calcd for $C_{20}H_{16}NSe$ $[M+H]^+$ 350.0443, found 350.0441.

1-Methyl-3-(phenanthren-9-yl)quinoline-2(1H)-selenone (96c)



According to **Procedure 10**, a solution of 0.431 g (1.00 mmol) of 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinoline-2(1H)-selenone **96c**.

Yield: 0.080 g (20%) of a red solid.

Mp: 271 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.73 (d, *J* = 8.0 Hz, 1H, 4′-H), 7.90 (s, 1H, 4-H), 7.87 (d, *J* = 7.8 Hz, 1H, 1′-H), 7.83 (d, *J* = 8.6 Hz, 1H, 8-H), 7.77 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 7.72 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H), 7.69-7.65 (m, 3H, 3′-H, 8′-H, 10′-H), 7.63 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1H, 6′-H), 7.60 (ddd, *J* = 1.0, 7.0, 7.9 Hz, 1H, 2′-H), 7.49-7.45 (m, 2H, 6-H, 7′-H), 4.61 (s, 3H, NCH_3) ppm.

^{13}C NMR (150 MHz, $CDCl_3$(deptq)[XL]): δ = 186.8 (-, C2), 146.2 (-, C3), 141.9 (-, C8a), 139.0 (-, C9′), 132.1 (+, C4), 131.9 (-, C10a′), 131.7 (+, C7), 131.3 (-, C8a′), 130.5 (-, C4a′), 130.5 (-, C4b′), 129.5 (+, C5), 129.0 (+, C1′), 127.5 (+, C9′), 127.1 (+, C8′),

[XXXIX] Using HRMS (ESI) measurements not give desired peaks
[XL] In this case was used DEPTQ spectrum for better determinations of atoms

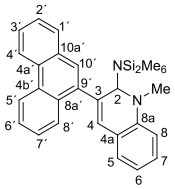
126.9 (+, C3′), 126.8 (+, C2′), 126.6 (+, C6′, C7′), 125.1 (+, C6), 125.0 (-, C4a), 123.1 (+, C5′), 122.9 (+, C4′), 116.5 (+, C8), 43.6 (+, N*C*H$_3$) ppm.

^{77}Se NMR (114 MHz, $CDCl_3$ + TMS) δ = 720.4 ppm.

IR (ATR): 1591, 1561, 1449, 1367, 1211, 1135, 1065, 908, 890, 759, 749, 740, 721, 611, 556, 488, 428 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{24}H_{17}NNaSe$ $[M+Na]^+$ 422.0413, found 422.0411.

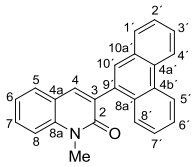
1-Methyl-3-(phenanthren-9-yl)-*N*,*N*-bis(trimethylsilyl)-1,2-dihydroquinolin-2-amine (100)



^{1}H NMR (600 MHz, THF-d_8): δ = 8.76 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.71 (d, *J* = 8.1 Hz, 1H, 4′-H), 8.18 (d, *J* = 8.1 Hz, 1H, 1′-H), 7.89 (s, 1H, 10′-H), 7.85 (d, *J* = 7.9 Hz, 1H, 8′-H), 7.60-7.56 (m, 2H, 3′-H, 6′-H), 7.53-7.49 (m, 2H, 2′-H, 7′-H), 7.17 (t, *J* = 7.8 Hz, 1H, 7-H), 7.13 (d, *J* = 7.1 Hz, 1H, 5-H), 6.81 (d, *J* = 8.1 Hz, 1H, 8-H), 6.76 (s, 1H, 4-H), 6.71 (t, *J* = 7.3 Hz, 1H, 6-H), 5.58 (s, 1H, 2-H), 3.19 (s, 3H, N*C*H_3), 0.00 (s, 18H, $NSi_2(CH_3)_6$) ppm.

^{13}C NMR (150 MHz, THF-d_8): δ = 141.5 (o, C8a), 136.9 (o, C9′), 133.1 (o, C3), 131.8 (o, C10a′), 131.0 (o, C8a′), 130.8 (o, C4a′), 130.0 (o, C4b′), 128.6 (+, C7), 128.4 (+, C8′), 127.4 (+, C10′), 126.51 (+, C1′), 126.46 (+, C7′), 126.42 (+, C4), 126.3 (+, C6′), 126.2 (+, C2′), 126.1 (+, C3′), 122.9 (+, C5), 122.4 (+, C4′), 121.1 (o, C4a), 116.9 (+, C6), 111.2 (+, C8), 83.6 (+, C2), 35.4 (+, N*C*H$_3$), 1.7 (+, $NSi_2(CH_3)_6$) ppm.

1-Methyl-3-(phenanthren-9-yl)quinolin-2(1*H*)-one (94)



Under a nitrogen atmosphere, 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate (0.431 g, 1.00 mmol), sulfur (0.128 g, 4.00 mmol) and LiOH (0.192 g, 8.00 mmol) were suspended in absolute toluene (10 mL), and then potassium *tert*-butoxide (0.896 g, 8.00 mmol) was added slowly with stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. After that, the mixture was concentrated *in vacuo*, and the crude product was purified by column chromatography with PE-EE as an eluent to give 1-methyl-3-(phenanthren-9-yl)quinolin-2(1H)-one **94**.

Yield: 0.184 g (55%) of a white solid.

Mp: 56 °C. (Lit. 55-58 °C)[102]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.72 (d, *J* = 8.0 Hz, 1H, 4′-H), 790 (s, 1H, 4-H), 7.88 (dd, *J* = 1.4, 7.8 Hz, 1H, 1′-H), 7.77-7.76 (m, 2H, 5′-H, 10-H), 7.68 (ddd, *J* = 1.4, 6.9, 8.3 Hz, 1H, 3′-H), 7.66-7.64 (m, 2H, 5-H, 7-H), 7.60 (ddd, *J* = 1.0, 6.9, 7.8 Hz, 1H, 2′-H), 7.53 (ddd, *J* = 1.2, 6.9, 8.2 Hz, 1H, 7′-H), 7.49 (d, *J* = 9.0 Hz, 1H, 8-H), 7.32-7.30 (m, 1H, 6-H), 3.86 (s, 3H, NCH_3) ppm.

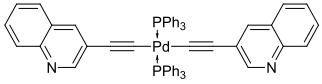
^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.0 (+, C2), 140.3 (o, C8a), 139.2 (+, C4), 134.3 (o, C9′), 133.3 (o, C3), 131.7 (o, C10a′), 130.8 (o, C4a′), 130.7 (+, C7), 130.6 (o, C4b′), 129.1 (+, C5), 128.9 (+,C1′), 128.4 (+, C10′), 127.0 (+, C3′), 126.79 (+, C8′), 126.77 (+, C2′), 126.73 (+, C7′), 126.68 (+, C6′), 123.1 (+, C5′), 122.7 (+, C4′), 122.5 (+, C6), 120.8 (o, C4a), 114.4 (+, C8), 30.2 (+, NCH_3) ppm.

IR (ATR): 3059, 1638, 1590, 1570, 1528, 1495, 1463, 1448, 1432, 1416, 1383, 1364, 1343, 1329, 1317, 1295, 1275, 1242, 1211, 1164, 1146, 1127, 1105, 1085, 1040, 1018, 1001, 979, 951, 927, 918, 899, 884, 861, 853, 805, 788, 769, 753, 748, 732, 721, 710, 660, 620, 615, 578, 558, 543, 509, 496, 482, 463, 454, 426, 416, 412, 407 cm^{-1}.

MS (ESI): *m/z* = 336.0 $[M+H]^+$.

Bis(triphenylphosphine)bis(quinolin-3-ylethynyl)palladium(II) (97)

A suspension of $Pd(PPh_3)_2Cl_2$ (0.140 g, 0.20 mmol) and CuI (0.002 g) in anhyd diethylamine was treated under a nitrogen atmosphere with 3-ethynylquinoline (0.153 g, 1.00 mmol) and then heated for 4 h under reflux temperature. The resulting precipitate was then filtered off, washed with ethyl acetate, ethanol, and water, and dried[XLI].



Yield: 0.186 g (99%) of an orange solid.

Mp: 179 °C. (Lit. 203 °C[103]).

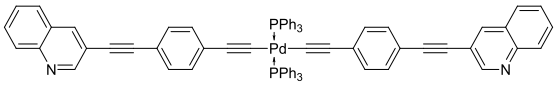
The compound is insoluble in all NMR solvents which were tested.

IR (ATR): 2104, 1956, 1588, 1567, 1479, 1433, 1406, 1336, 1182, 1098, 1027, 982, 955, 902, 858, 782, 743, 702, 688, 612, 537, 513, 474, 459, 423 cm^{-1}.

[XLI] Infrared spectrum is in agreement with those reported in the literature[103]

***Bis*(triphenylphosphine)bis((4-(quinolin-3-ylethynyl)phenyl)ethynyl)palladium(II) (98)**

A suspension of $Pd(PPh_3)_2Cl_2$ (0.081 g, 0.11 mmol) and CuI (0.002 g) in anhyd diethylamine was treated under a nitrogen atmosphere with 3-((4-ethynylphenyl)ethynyl)quinoline (0.127 g, 0.50 mmol) and then heated for 3 h under reflux temperature. The resulting precipitate was then filtered off, washed with ethyl acetate, ethanol, and water, and dried.



Yield: 0.076 g (58%) of a dark brown solid.

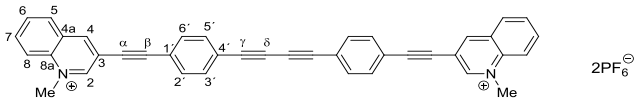
Mp: >200 °C (decomp.).

The compound is insoluble in all NMR solvents which we tested.

IR (ATR): 3057, 3037, 2206, 1911, 1617, 1599, 1566, 1487, 1403, 1348, 1101, 1015, 980, 946, 905, 861, 828, 783, 738, 641, 623, 543, 529, 469, 424 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{74}H_{51}N_2P_2Pd$ $[M+H]^+$ 1135.2557, found 1135.2650.

3,3'-(Buta-1,3-diyne-1,4-diylbis(benzene-4,1-diylethyne-2,1-diyl)bis(1-methylquinolinium) dihexafluorophosphate (99)



A sample of *bis*(triphenylphosphine)*bis*((4-(quinolin-3-ylethynyl)phenyl)ethynyl)

palladium(II) **98** (0.060 g, 0.055 mmol) was suspended in anhyd dichloromethane (10 mL) and then treated dropwise at 0 °C with methyl triflate (0.011 mL, 0.1 mmol). After 12 h, the resulting precipitate was filtered off and washed with dichloromethane and ethyl acetate. The complex was then dissolved in MeOH and treated with an aqueous solution of NH_4PF_6. The resulting precipitate was filtered off and washed with ethanol and diethyl ether to give **99**.

Yield: 0.046 g (100%) of an olive green solid.

Mp: 296 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.88 (s, 2H, 2-H), 9.52 (s, 2H, 4-H), 8.54 (d, *J* = 8.5 Hz, 2H, 8-H), 8.45 (d, *J* = 7.6 Hz, 2H, 5-H), 8.32 (t, *J* = 7.2 Hz, 2H, 7-H), 8.11 (t, *J* = 7.1 Hz, 2H, 6-H), 7.79 (d, *J* = 7.3 Hz, 4H, 3′-H, 5′-H), 7.75 (d, *J* = 7.3 Hz, 4H, 2′-H, 6′-H) 4.65 (s, 6H, NC*H*$_3$) ppm.

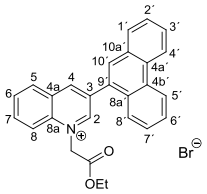
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.1 (+, C2), 148.2 (+, C4), 137.4 (o, C8a), 136.3 (+, C7), 133.1 (+, C3′, C5′), 132.1 (+, C2′, C6′), 130.7 (+, C6), 130.4 (+, C5), 128.7 (o, C4a), 122.0 (o, C1′), 121.7 (o, C4′), 119.3 (+, C8), 116.3 (o, C3), 93.9 (o, Cβ), 86.0 (o, Cα), 82.3 (o, Cγ), 75.6 (o, Cδ), 45.5 (+, N*C*H$_3$) ppm.

^{31}P NMR (243 MHz, DMSO-d_6): δ = -144.4 (sept, *J* = 709.2 Hz, PF_6) ppm.

IR (ATR): 3064, 3039, 2221, 1630, 1606, 1580, 1522, 1500, 1379, 1359, 1321, 1261, 1225, 1155, 1031, 972, 926, 834, 769, 756, 637, 557, 514, 431 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{40}H_{26}N_2$ $[M]^{2+}$ 267.1040, found 267.1032.

1-(2-Ethoxy-2-oxoethyl)-3-(phenanthren-9-yl)quinolinium bromide (92)



Samples of 0.305 g (1.00 mmol) of 3-(phenanthren-9-yl)quinoline were dissolved in toluene. Then 0.40 mL (1.25 mmol) of ethyl bromoacetate was added with stirring. Thereafter, the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 × 10 mL), and dried to afford the product.

Yield: 0.448 g (95%) of a maximum yellow colored solid.

Mp: 233 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.99 (d, *J* = 1.9 Hz, 1H, 2-H), 9.74 (d, *J* = 1.9 Hz, 1H, 4-H), 9.06 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.99 (d, *J* = 8.2 Hz, 1H, 4′-H), 8.62 (dd, *J* = 1.4, 8.6 Hz, 1H, 5-H), 8.60 (d, *J* = 9.2 Hz, 1H, 8-H), 8.37 (ddd, *J* = 1.6, 7.2, 8.9 Hz, 1H, 7-H), 8.20 (s, 1H, 10′-H), 8.16 (ddd, *J* = 0.7, 7.5, 7.7 Hz, 1H, 6-H), 8.13 (dd, *J* = 1.2, 7.8 Hz, 1H, 1′-H), 7.94 (dd, *J* = 0.8, 8.2 Hz, 1H, 8′-H), 7.85 (ddd, *J* = 1.2, 7.0, 8.3 Hz, 1H, 6′-H), 7.84 (ddd, *J* = 1.4, 7.0, 8.3 Hz, 1H, 3′-H), 7.78 (ddd, *J* = 0.9, 7.0, 7.8 Hz, 1H, 2′-H), 7.72 (ddd, *J* = 1.1, 7.0, 8.2 Hz, 1H, 7′-H), 6.29 (s, 2H, CH_2COO), 4.28 (q, *J* = 7.1 Hz, 2H, CH_2CH$_3$), 1.27 (t, *J* = 7.4 Hz, 3H, CH$_2$CH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 166.1 (o, *C*OO), 152.0 (+, C2), 148.7 (+, C4), 137.5 (o, C8a), 136.2 (+, C7), 133.3 (o, C3), 130.9 (+, C5), 130.6 (o, C9′), 130.5 (o, 10a′), 130.4 (+, C6), 130.3 (+, C10′), 130.2 (o, C4b′), 130.1 (C4a′), 129.4 (o, C4a), 129.2 (o, C8a′), 129.1 (+, C1′), 128.3 (+, C3′), 127.73 (+, C7′), 127.70 (+, C2′), 127.65

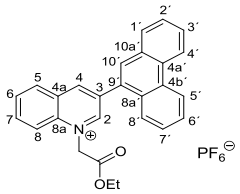
(+, C6′), 125.6 (+, C8′), 123.8 (+, C5′), 123.1 (+, C4′), 118.9 (+, C8), 62.4 (-, *C*$H_2$$CH_3$), 57.5 (-, *C*$H_2$COO), 14.0 (+, CH_2*C*H_3) ppm.

IR (ATR): 3051, 2971, 2903, 2843, 2717, 1964, 1737, 1526, 1453, 1374, 1212, 1007, 899, 856, 771, 750, 723, 654, 514, 429 cm^{-1}.

MS (ESI): *m/z* = 392.1 $[M]^+$.

HRMS (ESI): *m/z* calcd for $C_{27}H_{22}NO_2$ $[M]^+$ 392.1640, found 392. 392.1644.

1-(2-Ethoxy-2-oxoethyl)-3-(phenanthren-9-yl)quinolinium hexafluorophosphate (92PF_6)



According to **Procedure 5**, a suspension of 0.067 g (0.14 mmol) of 1-(2-ethoxy-2-oxoethyl)-3-(phenanthren-9-yl)quinolinium bromide **92** and 0.030 g (0.18 mmol) of NH_4PF_6 in 4 mL of water was stirred for 0.5 h at rt to give 1-(2-ethoxy-2-oxoethyl)-3-(phenanthren-9-yl)quinolinium hexafluorophosphate (**92PF_6**).

Yield: 0.065 g (85%) of a maximum yellow colored solid.

Mp: 211 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.99 (d, *J* = 1.9 Hz, 1H, 2-H), 9.74 (d, *J* = 1.9 Hz, 1H, 4-H), 9.06 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.99 (d, *J* = 8.2 Hz, 1H, 4′-H), 8.62 (dd, *J* = 1.4, 8.6 Hz, 1H, 5-H), 8.60 (d, *J* = 9.2 Hz, 1H, 8-H), 8.37 (ddd, *J* = 1.6, 7.2, 8.9 Hz, 1H, 7-

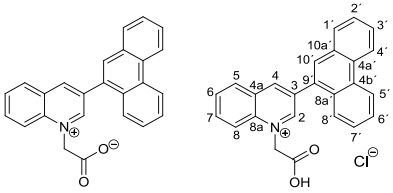
H), 8.20 (s, 1H, 10′-H), 8.16 (ddd, *J* = 0.7, 7.5, 7.7 Hz, 1H, 6-H), 8.13 (dd, *J* = 1.2, 7.8 Hz, 1H, 1′-H), 7.94 (dd, *J* = 0.8, 8.2 Hz, 1H, 8′-H), 7.85 (ddd, *J* = 1.2, 7.0, 8.3 Hz, 1H, 6′-H), 7.84 (ddd, *J* = 1.4, 7.0, 8.3 Hz, 1H, 3′-H), 7.78 (ddd, *J* = 0.9, 7.0, 7.8 Hz, 1H, 2′-H), 7.72 (ddd, *J* = 1.1, 7.0, 8.2 Hz, 1H, 7′-H), 6.29 (s, 2H, C*H*$_2$COO), 4.28 (q, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 1.27 (t, *J* = 7.4 Hz, 3H, CH$_2$C*H*$_3$) ppm.

^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ = 166.1 (o, *C*OO), 152.0 (+, C2), 148.7 (+, C4), 137.5 (o, C8a), 136.2 (+, C7), 133.3 (o, C3), 130.9 (+, C5), 130.6 (o, C9′), 130.5 (o, 10a′), 130.4 (+, C6), 130.3 (+, C10′), 130.2 (o, C4b′), 130.1 (C4a′), 129.4 (o, C4a), 129.2 (o, C8a′), 129.1 (+, C1′), 128.3 (+, C3′), 127.73 (+, C7′), 127.70 (+, C2′), 127.65 (+, C6′), 125.6 (+, C8′), 123.8 (+, C5′), 123.1 (+, C4′), 118.9 (+, C8), 62.4 (-, *C*H$_2$CH$_3$), 57.5 (-, *C*H$_2$COO), 14.0 (+, CH$_2$*C*H$_3$) ppm.

IR (ATR): 3051, 3013, 2972, 2901, 2841, 1738, 1577, 1526, 1495, 1453, 1434, 1389, 1374, 1324, 1213, 1094, 1063, 1008, 987, 923, 900, 840, 776, 766, 752, 724, 655, 632, 616, 600, 593, 558, 538, 514, 495, 442, 431 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{27}H_{22}NO_2$ $[M]^+$ 392.1640, found 392.1649.

(3-(Phenanthren-9-yl)quinolinium-1-yl)acetate (93)



A solution of 0.236 g (0.50 mmol) of 1-(2-ethoxy-2-oxoethyl)-3-(phenanthren-9-yl)quinolinium bromide **92** and 0.200 g (5.00 mmol) of NaOH in 25 mL of the methanol-water mixture was stirred for 12 h at rt. Then, the solution was acidified (pH = 1) and then concentrated *in vacuo*. Finally, a purification by column

chromatography (methanol: chloroform = 1:3) gave (3-(phenanthren-9-yl)quinolinium-1-yl)acetate **93**.

Yield: 0.118 g (65%) of a yellow solid.

Mp: 216 °C (decomp.).

IR (ATR): 3029, 1634, 1522, 1339, 919, 887, 777, 749, 724, 655, 616, 541, 519, 429 cm^{-1}.

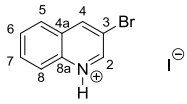
HRMS (ESI): *m/z* calcd for $C_{25}H_{17}NNaO_2$ $[M+Na]^+$ 386.1157, found 386.1159.

1-(Carboxymethyl)-3-(phenanthren-9-yl)quinolinium chloride

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.04 (d, *J* = 1.9 Hz, 1H, 2-H), 9.70 (s, 1H, 4-H), 9.05 (d, *J* = 8.3 Hz, 1H, 5′-H), 8.97 (d, *J* = 8.3 Hz, 1H, 4′-H), 8.61 (d, *J* = 8.2 Hz, 1H, 5-H), 8.58 (d, *J* = 9.0 Hz, 1H, 8-H), 8.36 (ddd, *J* = 1.5, 7.2, 8.8 Hz, 1H, 7-H), 8.18 (s, 1H, 10′-H), 8.14 (t, *J* = 7.7 Hz, 1H, 6-H), 8.12 (d, *J* = 7.6 Hz, 1H, 1′-H), 7.92 (d, *J* = 8.2 Hz, 1H, 8′-H), 7.84 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H, 6′-H), 7.84 (ddd, *J* = 1.4, 7.2, 8.3 Hz, 1H, 3′-H), 7.77 (t, *J* = 7.4 Hz, 1H, 2′-H), 7.71 (t, *J* = 7.8 Hz, 1H, 7′-H), 6.21 (s, 2H, C*H*$_2$COO) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 167.2 (o, *C*OO), 151.8 (+, C2), 148.4 (+, C4), 137.6 (o, C8a), 136.1 (+, C7), 133.3 (o, C3), 130.9 (+, C5), 130.64 (o, C9′), 130.56 (o, 10a′), 130.4 (+, C6), 130.3 (+, C10′), 130.3 (o, C4b′), 130.2 (C4a′), 129.4 (o, C4a), 129.3 (o, C8a′), 129.1 (+, C1′), 128.3 (+, C3′), 127.76 (+, C7′), 127.71 (+, C2′), 127.67 (+, C6′), 125.6 (+, C8′), 123.8 (+, C5′), 123.1 (+, C4′), 118.8 (+, C8), 57.8 (-, *C*H$_2$COO) ppm.

3-Bromoquinolinium iodide



3-Bromoquinoline **33a** (0.36 mL, 1.00 mmol) was dissolved in toluene. Then 0.13 mL (1.10 mmol) of 2-iodo-2-methylpropane was added with stirring. Thereafter, the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 × 10 mL), and dried to afford the product.

Yield: 0.336 g (100%) of a green solid.

Mp: 142 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.05 (d, *J* = 2.3 Hz, 1H, 2-H), 8.86 (d, *J* = 2.3 Hz, 1H, 4-H), 8.06 (d, *J* = 8.6 Hz, 1H, 8-H), 8.03 (d, *J* = 8.0 Hz, 1H, 5-H), 7.87 (ddd, *J* = 1.5, 6.9, 8.6 Hz, 1H, 7-H), 7.72 (ddd, *J* = 1.5, 6.9, 8.0 Hz, 1H, 6-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.4 (+, C2), 144.3 (o, C8a), 139.1 (+, C4), 130.9 (+, C7), 128.9 (o, C4a), 128.3 (+, C6), 127.7 (+, C5), 127.6 (+, C8), 116.5 (o, C3) ppm.

IR (ATR): 1542, 1349, 1202, 1096, 971, 944, 831, 762, 751, 629, 603, 582, 520, 464 cm^{-1}.

MS (ESI): *m/z* = 207.9 $[M]^+$, 126.9 $[Iodide]^-$.

HRMS (ESI): *m/z* calcd for C_9H_7BrN $[M]^+$ 207.9762, found 207.9760.

5.5 X-ray analysis data

Crystal structure determination of 3-(3-hydroxy-1-oxo-1H-inden-2-yl)-1-methylquinolin-1-ium chloride 50×HCl

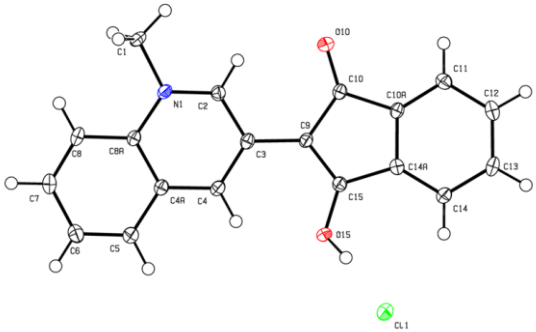


Figure 36: X-ray structure of molecules **50×HCl**

Table 2: Crystallography data for **50×HCl**

$C_{19}H_{14}NO_2 \cdot Cl$	$F(000)$ = 672
M_r = 323.76	D_x = 1.487 Mg m^{-3}
Monoclinic, $P2_1/c$ *(no.14)*	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 10.2551 (4) Å	Cell parameters from 9888 reflections
b = 6.3701 (2) Å	θ = 4.0–72.1°
c = 22.6746 (8) Å	μ = 2.42 mm^{-1}
β = 102.474 (2)°	T = 123 K
V = 1446.28 (9) Å^3	Plates, orange
Z = 4	0.36 × 0.08 × 0.02 mm

Table 3: Data collection for **50×HCl**

Bruker D8 Venture diffractometer with Photon100 detector	2600 reflections with $I > 2\sigma(I)$
Radiation source: IμS microfocus	R_{int} = 0.044
rotation in ϕ and ω, 1°, shutterless scans	θ_{max} = 72.1°, θ_{min} = 4.0°

Table 3 (continued).

Absorption correction: multi-scan *SADABS* (Sheldrick, 2015)	h = -12→12
T_{min} = 0.751, T_{max} = 0.958	k = -7→7
19704 measured reflections	l = -27→27
2814 independent reflections	

Table 4: Refinement for **50×HCl**

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.049	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.145	H atoms treated by a mixture of independent and constrained refinement
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.085P)^2 + 1.750P]$ where $P = (F_o^2 + 2F_c^2)/3$
2814 reflections	$(\Delta/\sigma)_{max} < 0.001$
212 parameters	$\Delta\rangle_{max}$ = 0.60 e Å^{-3}
1 restraint	$\Delta\rangle_{min}$ = -0.50 e Å^{-3}

Computing details

Data collection: *APEX2*; cell refinement: *SAINT*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXD*; program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 1 deg., 12+1 runs, 2326 frames, 20/25/30/35/40 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for

estimating esds involving l.s. planes.

Table 5: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **50×HCl**

	X	*Y*	*z*	U_{iso}*/U_{eq}
Cl1	0.24181 (5)	0.38809 (9)	0.11269 (3)	0.0220 (2)
C1	1.1024 (2)	0.8809 (4)	0.15043 (11)	0.0180 (5)
H1A	1.1420	0.7737	0.1799	0.027*
H1B	1.0995	1.0154	0.1711	0.027*
H1C	1.1565	0.8957	0.1200	0.027*
N1	0.96546 (18)	0.8175 (3)	0.12079 (8)	0.0139 (4)
C2	0.9153 (2)	0.6433 (3)	0.13961 (10)	0.0142 (4)
H2	0.9692	0.5650	0.1714	0.017*
C3	0.7857 (2)	0.5702 (4)	0.11445 (9)	0.0139 (4)
C4	0.7106 (2)	0.6877 (4)	0.06756 (10)	0.0149 (5)
H4	0.6236	0.6415	0.0485	0.018*
C4A	0.7614 (2)	0.8736 (3)	0.04793 (10)	0.0138 (5)
C5	0.6847 (2)	0.9983 (4)	0.00132 (10)	0.0175 (5)
H5	0.5974	0.9543	-0.0181	0.021*
C6	0.7351 (2)	1.1814 (4)	-0.01601 (10)	0.0193 (5)
H6	0.6822	1.2654	-0.0468	0.023*
C7	0.8657 (2)	1.2457 (4)	0.01183 (10)	0.0189 (5)
H7	0.9000	1.3726	-0.0008	0.023*
C8	0.9441 (2)	1.1287 (4)	0.05669 (10)	0.0168 (5)
H8	1.0321	1.1730	0.0749	0.020*
C8A	0.8917 (2)	0.9419 (4)	0.07526 (9)	0.0132 (4)
C9	0.7351 (2)	0.3810 (3)	0.13805 (9)	0.0134 (5)
C10	0.8136 (2)	0.2365 (3)	0.18264 (9)	0.0133 (4)
O10	0.93238 (16)	0.2469 (3)	0.20750 (7)	0.0185 (4)
C10A	0.7198 (2)	0.0674 (3)	0.19355 (9)	0.0137 (4)
C11	0.7439 (2)	-0.1082 (4)	0.22931 (10)	0.0166 (5)
H11	0.8301	-0.1371	0.2532	0.020*
C12	0.6357 (2)	-0.2433 (4)	0.22906 (10)	0.0189 (5)
H12	0.6489	-0.3661	0.2534	0.023*
C13	0.5100 (2)	-0.2018 (4)	0.19415 (10)	0.0177 (5)
H13	0.4388	-0.2969	0.1944	0.021*
C14	0.4872 (2)	-0.0191 (4)	0.15829 (10)	0.0157 (5)
H14	0.4011	0.0114	0.1344	0.019*
C14A	0.5930 (2)	0.1134 (3)	0.15889 (9)	0.0137 (5)
C15	0.6051 (2)	0.3114 (3)	0.12568 (9)	0.0136 (4)
O15	0.50475 (16)	0.4028 (3)	0.08898 (8)	0.0194 (4)
H15	0.425 (2)	0.381 (5)	0.0950 (14)	0.029*

Table 6: Atomic displacement parameters (Å^2) for **50×HCl**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0159 (3)	0.0204 (3)	0.0290 (3)	-0.0025 (2)	0.0035 (2)	0.0040 (2)
C1	0.0106 (11)	0.0188 (12)	0.0236 (11)	-0.0036 (9)	0.0016 (9)	0.0002 (9)
N1	0.0106 (9)	0.0144 (9)	0.0168 (9)	-0.0018 (7)	0.0031 (7)	-0.0006 (7)
C2	0.0138 (10)	0.0130 (10)	0.0163 (10)	0.0003 (8)	0.0044 (8)	0.0007 (8)
C3	0.0137 (11)	0.0135 (10)	0.0155 (10)	-0.0012 (8)	0.0055 (8)	-0.0015 (8)
C4	0.0128 (10)	0.0147 (11)	0.0172 (10)	-0.0023 (8)	0.0033 (8)	-0.0009 (8)
C4A	0.0141 (11)	0.0127 (11)	0.0151 (10)	-0.0007 (8)	0.0045 (8)	-0.0015 (8)
C5	0.0167 (11)	0.0175 (11)	0.0177 (10)	-0.0016 (9)	0.0026 (8)	0.0010 (9)
C6	0.0236 (12)	0.0159 (11)	0.0185 (11)	-0.0003 (9)	0.0043 (9)	0.0021 (9)
C7	0.0232 (12)	0.0143 (11)	0.0211 (11)	-0.0030 (9)	0.0089 (9)	0.0013 (9)
C8	0.0167 (11)	0.0148 (11)	0.0206 (11)	-0.0054 (9)	0.0077 (9)	-0.0017 (8)
C8A	0.0128 (11)	0.0132 (10)	0.0144 (10)	-0.0015 (8)	0.0047 (8)	-0.0009 (8)
C9	0.0122 (10)	0.0125 (11)	0.0155 (10)	-0.0019 (8)	0.0029 (8)	-0.0003 (8)
C10	0.0144 (11)	0.0116 (10)	0.0143 (10)	-0.0011 (8)	0.0041 (8)	-0.0019 (8)
O10	0.0138 (8)	0.0188 (9)	0.0212 (8)	-0.0016 (6)	-0.0001 (6)	0.0019 (6)
C10A	0.0147 (11)	0.0116 (10)	0.0151 (10)	-0.0020 (8)	0.0040 (8)	-0.0020 (8)
C11	0.0180 (11)	0.0163 (11)	0.0150 (10)	0.0010 (9)	0.0024 (8)	0.0008 (8)
C12	0.0255 (13)	0.0145 (11)	0.0180 (11)	-0.0004 (9)	0.0073 (9)	0.0029 (8)
C13	0.0191 (12)	0.0146 (11)	0.0213 (11)	-0.0060 (9)	0.0083 (9)	-0.0016 (9)
C14	0.0140 (10)	0.0160 (11)	0.0174 (10)	-0.0014 (9)	0.0041 (8)	-0.0006 (9)
C14A	0.0162 (11)	0.0127 (11)	0.0128 (10)	-0.0001 (8)	0.0042 (8)	-0.0006 (8)
C15	0.0134 (10)	0.0115 (10)	0.0163 (10)	0.0007 (8)	0.0041 (8)	-0.0004 (8)
O15	0.0098 (8)	0.0221 (9)	0.0253 (9)	-0.0011 (6)	0.0015 (6)	0.0080 (7)

Table 7: Bond lengths (Å) for **50×HCl**

C1—N1	1.476 (3)	C8—C8A	1.408 (3)
C1—H1A	0.9800	C8—H8	0.9500
C1—H1B	0.9800	C9—C15	1.375 (3)
C1—H1C	0.9800	C9—C10	1.472 (3)
N1—C2	1.332 (3)	C10—O10	1.228 (3)
N1—C8A	1.389 (3)	C10—C10A	1.500 (3)
C2—C3	1.407 (3)	C10A—C11	1.372 (3)
C2—H2	0.9500	C10A—C14A	1.398 (3)
C3—C4	1.389 (3)	C11—C12	1.404 (3)
C3—C9	1.458 (3)	C11—H11	0.9500
C4—C4A	1.404 (3)	C12—C13	1.384 (3)
C4—H4	0.9500	C12—H12	0.9500
C4A—C8A	1.415 (3)	C13—C14	1.410 (3)
C4A—C5	1.417 (3)	C13—H13	0.9500
C5—C6	1.367 (3)	C14—C14A	1.372 (3)
C5—H5	0.9500	C14—H14	0.9500
C6—C7	1.412 (3)	C14A—C15	1.488 (3)
C6—H6	0.9500	C15—O15	1.312 (3)
C7—C8	1.372 (3)	O15—H15	0.870 (18)
C7—H7	0.9500		

Table 8: Bond angles (º) for **50×HCl**

N1—C1—H1A	109.5	C8A—C8—H8	120.7
N1—C1—H1B	109.5	N1—C8A—C8	121.5 (2)
H1A—C1—H1B	109.5	N1—C8A—C4A	117.50 (19)
N1—C1—H1C	109.5	C8—C8A—C4A	121.0 (2)
H1A—C1—H1C	109.5	C15—C9—C3	126.7 (2)
H1B—C1—H1C	109.5	C15—C9—C10	107.50 (19)
C2—N1—C8A	121.83 (19)	C3—C9—C10	125.7 (2)
C2—N1—C1	118.54 (19)	O10—C10—C9	128.5 (2)
C8A—N1—C1	119.62 (18)	O10—C10—C10A	124.8 (2)
N1—C2—C3	122.8 (2)	C9—C10—C10A	106.68 (18)
N1—C2—H2	118.6	C11—C10A—C14A	122.0 (2)
C3—C2—H2	118.6	C11—C10A—C10	130.0 (2)
C4—C3—C2	116.8 (2)	C14A—C10A—C10	108.00 (19)
C4—C3—C9	122.9 (2)	C10A—C11—C12	117.1 (2)
C2—C3—C9	120.3 (2)	C10A—C11—H11	121.4
C3—C4—C4A	121.0 (2)	C12—C11—H11	121.4
C3—C4—H4	119.5	C13—C12—C11	121.5 (2)
C4A—C4—H4	119.5	C13—C12—H12	119.2
C4—C4A—C8A	120.0 (2)	C11—C12—H12	119.2
C4—C4A—C5	121.7 (2)	C12—C13—C14	120.4 (2)
C8A—C4A—C5	118.3 (2)	C12—C13—H13	119.8
C6—C5—C4A	120.6 (2)	C14—C13—H13	119.8
C6—C5—H5	119.7	C14A—C14—C13	118.0 (2)
C4A—C5—H5	119.7	C14A—C14—H14	121.0
C5—C6—C7	120.0 (2)	C13—C14—H14	121.0
C5—C6—H6	120.0	C14—C14A—C10A	121.0 (2)
C7—C6—H6	120.0	C14—C14A—C15	132.0 (2)
C8—C7—C6	121.4 (2)	C10A—C14A—C15	107.02 (19)
C8—C7—H7	119.3	O15—C15—C9	125.4 (2)
C6—C7—H7	119.3	O15—C15—C14A	123.9 (2)
C7—C8—C8A	118.7 (2)	C9—C15—C14A	110.72 (19)
C7—C8—H8	120.7	C15—O15—H15	118 (2)

Table 9: Torsion angles (º) for **50×HCl**

C8A—N1—C2—C3	1.1 (3)	C15—C9—C10—O10	-176.8 (2)
C1—N1—C2—C3	179.7 (2)	C3—C9—C10—O10	-0.1 (4)
N1—C2—C3—C4	0.8 (3)	C15—C9—C10—C10A	2.7 (2)
N1—C2—C3—C9	-178.4 (2)	C3—C9—C10—C10A	179.40 (19)
C2—C3—C4—C4A	-1.9 (3)	O10—C10—C10A—C11	-3.1 (4)
C9—C3—C4—C4A	177.3 (2)	C9—C10—C10A—C11	177.4 (2)
C3—C4—C4A—C8A	1.2 (3)	O10—C10—C10A—C14A	177.8 (2)
C3—C4—C4A—C5	-178.2 (2)	C9—C10—C10A—C14A	-1.7 (2)
C4—C4A—C5—C6	178.4 (2)	C14A—C10A—C11—C12	1.0 (3)
C8A—C4A—C5—C6	-1.0 (3)	C10—C10A—C11—C12	-178.0 (2)
C4A—C5—C6—C7	1.3 (3)	C10A—C11—C12—C13	0.2 (3)
C5—C6—C7—C8	-0.5 (4)	C11—C12—C13—C14	-0.9 (3)

Table 10: (continued).

C6—C7—C8—C8A	-0.5 (3)	C12—C13—C14—C14A	0.5 (3)
C2—N1—C8A—C8	178.3 (2)	C13—C14—C14A—C10A	0.6 (3)
C1—N1—C8A—C8	-0.3 (3)	C13—C14—C14A—C15	177.7 (2)
C2—N1—C8A—C4A	-1.9 (3)	C11—C10A—C14A—C14	-1.4 (3)
C1—N1—C8A—C4A	179.53 (19)	C10—C10A—C14A—C14	177.79 (19)
C7—C8—C8A—N1	-179.4 (2)	C11—C10A—C14A—C15	-179.1 (2)
C7—C8—C8A—C4A	0.8 (3)	C10—C10A—C14A—C15	0.1 (2)
C4—C4A—C8A—N1	0.7 (3)	C3—C9—C15—O15	1.7 (4)
C5—C4A—C8A—N1	-179.88 (19)	C10—C9—C15—O15	178.3 (2)
C4—C4A—C8A—C8	-179.4 (2)	C3—C9—C15—C14A	-179.4 (2)
C5—C4A—C8A—C8	0.0 (3)	C10—C9—C15—C14A	-2.8 (2)
C4—C3—C9—C15	-11.3 (4)	C14—C14A—C15—O15	3.3 (4)
C2—C3—C9—C15	167.9 (2)	C10A—C14A—C15—O15	-179.3 (2)
C4—C3—C9—C10	172.7 (2)	C14—C14A—C15—C9	-175.6 (2)
C2—C3—C9—C10	-8.2 (3)	C10A—C14A—C15—C9	1.7 (2)

Table 10: Hydrogen-bond geometry (Å, º) for **50×HCl**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···O10^{i}	0.98	2.53	3.336 (3)	139
C2—H2···O10	0.95	2.25	2.943 (3)	129
C8—H8···Cl1^{ii}	0.95	2.54	3.462 (2)	164
O15—H15···Cl1	0.87 (2)	2.00 (2)	2.8626 (17)	169 (3)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*+1, *z*.

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Crystal structure determination of 3-((4-(methoxycarbonyl)-phenyl)ethynyl)-1-methylquinolin-1-ium hexafluorophosphate 42aPF$_6$, acetonitrile

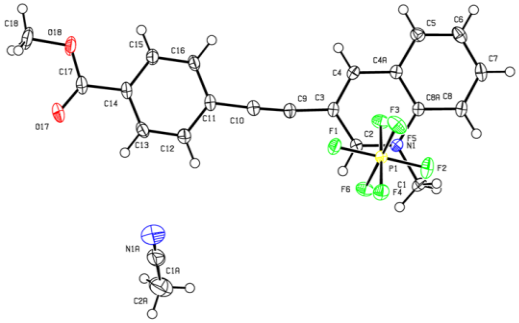

Figure 37: X-ray structure of molecules **42aPF$_6$**

Table 11: Crystallography data for **42aPF$_6$**

$C_{20}H_{16}NO_2 \cdot F_6P \cdot C_2H_3N$	$F(000) = 1000$
$M_r = 488.36$	$D_x = 1.471$ Mg m^{-3}
Monoclinic, $P2_1/c$ *(no.14)*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.5730$ (7) Å	Cell parameters from 9394 reflections
$b = 8.1725$ (3) Å	$\theta = 2.5–27.5°$
$c = 17.7139$ (8) Å	$\mu = 0.20$ mm^{-1}
$\beta = 101.950$ (2)°	$T = 123$ K
$V = 2205.60$ (16) Å^3	Plates, colourless
$Z = 4$	0.36 × 0.20 × 0.10 mm

Table 12: Data collection for **42aPF$_6$**

Bruker D8 VENTURE diffractometer with Photon100 detector	5097 independent reflections
Radiation source: INCOATEC microfocus sealed tube	4628 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.029$
rotation in ϕ and ω, 1°, shutterless scans	$\theta_{max} = 27.6°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan	$h = -20 \rightarrow 20$
SADABS (Sheldrick, 2014)	
$T_{min} = 0.924$, $T_{max} = 0.977$	$k = -10 \rightarrow 10$
67004 measured reflections	$l = -22 \rightarrow 23$

Table 13: Refinement for **42aPF$_6$**

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 1.1246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
5097 reflections	$\Delta\rangle_{max} = 0.38$ e Å^{-3}
302 parameters	$\Delta\rangle_{min} = -0.30$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0048 (6)

Computing details

Data collection: *APEX3*; cell refinement: *APEX3*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 1 deg., 7+1 runs, 1024 frames, 16 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 14: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **42aPF$_6$**

	X	*Y*	*z*	U_{iso}*/U_{eq}
C1	0.37756 (9)	0.08290 (15)	0.28223 (7)	0.0213 (3)
H1A	0.4159	0.1048	0.2460	0.032*
H1B	0.3227	0.1443	0.2664	0.032*
H1C	0.3646	-0.0344	0.2823	0.032*
N1	0.42215 (6)	0.13450 (12)	0.36092 (6)	0.0152 (2)
C2	0.49923 (8)	0.20924 (14)	0.36968 (7)	0.0167 (2)
H2	0.5256	0.2213	0.3262	0.020*
C3	0.54303 (7)	0.27109 (14)	0.44132 (7)	0.0171 (2)
C4	0.50405 (8)	0.25305 (15)	0.50401 (7)	0.0184 (2)
H4	0.5321	0.2954	0.5529	0.022*
C4A	0.42292 (8)	0.17210 (14)	0.49580 (7)	0.0169 (2)
C5	0.38176 (8)	0.14952 (16)	0.55917 (7)	0.0218 (3)
H5	0.4090	0.1897	0.6087	0.026*
C6	0.30301 (9)	0.07031 (17)	0.54954 (8)	0.0256 (3)
H6	0.2757	0.0557	0.5923	0.031*
C7	0.26238 (8)	0.01043 (17)	0.47660 (8)	0.0259 (3)
H7	0.2078	-0.0449	0.4708	0.031*
C8	0.29982 (8)	0.03003 (15)	0.41341 (8)	0.0211 (3)
H8	0.2714	-0.0107	0.3644	0.025*
C8A	0.38098 (7)	0.11136 (14)	0.42249 (7)	0.0157 (2)
C9	0.62515 (8)	0.35402 (15)	0.44875 (7)	0.0203 (2)
C10	0.69375 (8)	0.42510 (15)	0.46163 (8)	0.0213 (3)
C11	0.77515 (8)	0.51229 (15)	0.48111 (8)	0.0205 (3)
C12	0.82500 (9)	0.54435 (17)	0.42559 (8)	0.0251 (3)
H12	0.8059	0.5058	0.3743	0.030*
C13	0.90220 (8)	0.63236 (17)	0.44567 (8)	0.0253 (3)
H13	0.9361	0.6538	0.4079	0.030*
C14	0.93055 (8)	0.68959 (16)	0.52049 (8)	0.0217 (3)
C15	0.88157 (8)	0.65682 (17)	0.57638 (8)	0.0244 (3)
H15	0.9012	0.6949	0.6277	0.029*
C16	0.80411 (8)	0.56845 (17)	0.55670 (8)	0.0236 (3)
H16	0.7706	0.5460	0.5947	0.028*
C17	1.01307 (8)	0.78748 (17)	0.53905 (8)	0.0257 (3)
O17	1.05593 (6)	0.82610 (14)	0.49231 (7)	0.0343 (2)
O18	1.03395 (7)	0.82926 (15)	0.61340 (6)	0.0373 (3)
C18	1.11361 (11)	0.9241 (3)	0.63579 (10)	0.0470 (5)
H18A	1.1641	0.8571	0.6302	0.071*
H18B	1.1203	0.9585	0.6897	0.071*
H18C	1.1104	1.0209	0.6027	0.071*
P1	0.35389 (2)	0.57545 (4)	0.28138 (2)	0.01576 (9)
F1	0.43538 (5)	0.69960 (9)	0.30703 (4)	0.02557 (18)
F2	0.27444 (5)	0.45103 (10)	0.25570 (5)	0.0318 (2)
F3	0.38074 (5)	0.48486 (9)	0.36288 (4)	0.02455 (17)
F4	0.32847 (5)	0.66889 (10)	0.20059 (4)	0.02662 (18)
F5	0.29208 (6)	0.69661 (10)	0.31688 (5)	0.0311 (2)
F6	0.41725 (5)	0.45549 (10)	0.24614 (4)	0.02636 (18)

Table 14 (continued).

	X	*Y*	*z*	U_{iso}*/U_{eq}
N1A	0.88436 (13)	0.5557 (3)	0.25137 (10)	0.0618 (5)
C1A	0.90232 (11)	0.4378 (3)	0.22373 (10)	0.0439 (4)
C2A	0.92269 (13)	0.2887 (3)	0.18720 (11)	0.0553 (5)
H2A1	0.8728	0.2133	0.1815	0.083*
H2A2	0.9747	0.2376	0.2191	0.083*
H2A3	0.9343	0.3142	0.1362	0.083*

Table 15: Atomic displacement parameters (Å^2) for **42aPF$_6$**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0248 (6)	0.0188 (6)	0.0181 (6)	-0.0030 (5)	-0.0003 (5)	-0.0028 (5)
N1	0.0162 (5)	0.0121 (4)	0.0165 (5)	0.0006 (4)	0.0013 (4)	-0.0002 (4)
C2	0.0160 (5)	0.0142 (5)	0.0206 (6)	0.0008 (4)	0.0051 (4)	0.0012 (4)
C3	0.0133 (5)	0.0147 (5)	0.0224 (6)	-0.0010 (4)	0.0015 (4)	0.0007 (4)
C4	0.0176 (5)	0.0173 (5)	0.0186 (5)	-0.0007 (4)	-0.0001 (4)	-0.0002 (4)
C4A	0.0162 (5)	0.0145 (5)	0.0192 (6)	0.0009 (4)	0.0019 (4)	0.0024 (4)
C5	0.0228 (6)	0.0230 (6)	0.0196 (6)	0.0010 (5)	0.0046 (5)	0.0034 (5)
C6	0.0230 (6)	0.0275 (7)	0.0287 (7)	0.0016 (5)	0.0108 (5)	0.0094 (5)
C7	0.0167 (6)	0.0245 (6)	0.0366 (7)	-0.0038 (5)	0.0058 (5)	0.0061 (5)
C8	0.0163 (5)	0.0187 (6)	0.0270 (6)	-0.0030 (4)	0.0010 (5)	0.0009 (5)
C8A	0.0149 (5)	0.0123 (5)	0.0193 (6)	0.0011 (4)	0.0023 (4)	0.0024 (4)
C9	0.0183 (6)	0.0189 (6)	0.0237 (6)	-0.0019 (5)	0.0042 (5)	0.0001 (5)
C10	0.0181 (6)	0.0204 (6)	0.0257 (6)	-0.0010 (5)	0.0051 (5)	0.0003 (5)
C11	0.0141 (5)	0.0180 (6)	0.0295 (7)	-0.0018 (4)	0.0044 (5)	0.0018 (5)
C12	0.0226 (6)	0.0267 (7)	0.0267 (7)	-0.0048 (5)	0.0070 (5)	-0.0031 (5)
C13	0.0206 (6)	0.0284 (7)	0.0296 (7)	-0.0043 (5)	0.0115 (5)	0.0011 (5)
C14	0.0134 (5)	0.0219 (6)	0.0296 (7)	-0.0032 (5)	0.0039 (5)	0.0042 (5)
C15	0.0189 (6)	0.0293 (7)	0.0241 (6)	-0.0061 (5)	0.0027 (5)	0.0030 (5)
C16	0.0173 (6)	0.0278 (7)	0.0267 (6)	-0.0054 (5)	0.0068 (5)	0.0034 (5)
C17	0.0154 (6)	0.0273 (7)	0.0337 (7)	-0.0047 (5)	0.0034 (5)	0.0065 (6)
O17	0.0226 (5)	0.0405 (6)	0.0427 (6)	-0.0121 (4)	0.0132 (4)	0.0017 (5)
O18	0.0237 (5)	0.0546 (7)	0.0302 (5)	-0.0225 (5)	-0.0020 (4)	0.0066 (5)
C18	0.0286 (8)	0.0642 (12)	0.0423 (9)	-0.0287 (8)	-0.0065 (7)	0.0066 (8)
P1	0.01509 (15)	0.01508 (15)	0.01706 (16)	0.00072 (11)	0.00320 (11)	0.00064 (11)
F1	0.0237 (4)	0.0248 (4)	0.0259 (4)	-0.0076 (3)	-0.0003 (3)	-0.0003 (3)
F2	0.0225 (4)	0.0251 (4)	0.0440 (5)	-0.0079 (3)	-0.0019 (3)	0.0032 (4)
F3	0.0311 (4)	0.0235 (4)	0.0198 (4)	0.0051 (3)	0.0071 (3)	0.0056 (3)
F4	0.0271 (4)	0.0292 (4)	0.0211 (4)	0.0002 (3)	-0.0008 (3)	0.0071 (3)
F5	0.0341 (4)	0.0232 (4)	0.0416 (5)	0.0107 (3)	0.0210 (4)	0.0042 (3)
F6	0.0305 (4)	0.0256 (4)	0.0253 (4)	0.0073 (3)	0.0112 (3)	-0.0025 (3)
N1A	0.0642 (11)	0.0780 (13)	0.0429 (9)	-0.0064 (10)	0.0102 (8)	-0.0070 (9)
C1A	0.0320 (8)	0.0717 (13)	0.0277 (8)	-0.0041 (8)	0.0054 (6)	0.0050 (8)
C2A	0.0478 (10)	0.0778 (14)	0.0428 (10)	0.0145 (10)	0.0151 (8)	0.0050 (10)

Table 16: Bond lengths (Å) for **42aPF$_6$**

C1—N1	1.4840 (15)	C12—C13	1.3827 (18)
C1—H1A	0.9800	C12—H12	0.9500
C1—H1B	0.9800	C13—C14	1.3885 (19)
C1—H1C	0.9800	C13—H13	0.9500
N1—C2	1.3270 (15)	C14—C15	1.3952 (18)
N1—C8A	1.3878 (15)	C14—C17	1.4915 (17)
C2—C3	1.4045 (16)	C15—C16	1.3871 (17)
C2—H2	0.9500	C15—H15	0.9500
C3—C4	1.3792 (17)	C16—H16	0.9500
C3—C9	1.4292 (16)	C17—O17	1.2081 (17)
C4—C4A	1.4068 (16)	C17—O18	1.3339 (18)
C4—H4	0.9500	O18—C18	1.4468 (16)
C4A—C5	1.4154 (17)	C18—H18A	0.9800
C4A—C8A	1.4171 (16)	C18—H18B	0.9800
C5—C6	1.3658 (18)	C18—H18C	0.9800
C5—H5	0.9500	P1—F2	1.5934 (8)
C6—C7	1.404 (2)	P1—F5	1.5978 (8)
C6—H6	0.9500	P1—F4	1.5980 (8)
C7—C8	1.3743 (19)	P1—F3	1.5991 (8)
C7—H7	0.9500	P1—F6	1.6061 (8)
C8—C8A	1.4074 (16)	P1—F1	1.6147 (8)
C8—H8	0.9500	N1A—C1A	1.142 (3)
C9—C10	1.1956 (18)	C1A—C2A	1.445 (3)
C10—C11	1.4328 (16)	C2A—H2A1	0.9800
C11—C12	1.3981 (18)	C2A—H2A2	0.9800
C11—C16	1.3990 (18)	C2A—H2A3	0.9800

Table 17: Bond angles (º) for **42aPF$_6$**

N1—C1—H1A	109.5	C12—C13—C14	120.56 (12)
N1—C1—H1B	109.5	C12—C13—H13	119.7
H1A—C1—H1B	109.5	C14—C13—H13	119.7
N1—C1—H1C	109.5	C13—C14—C15	120.02 (11)
H1A—C1—H1C	109.5	C13—C14—C17	118.71 (12)
H1B—C1—H1C	109.5	C15—C14—C17	121.27 (12)
C2—N1—C8A	121.65 (10)	C16—C15—C14	119.76 (12)
C2—N1—C1	118.47 (10)	C16—C15—H15	120.1
C8A—N1—C1	119.80 (10)	C14—C15—H15	120.1
N1—C2—C3	121.98 (11)	C15—C16—C11	120.17 (12)
N1—C2—H2	119.0	C15—C16—H16	119.9
C3—C2—H2	119.0	C11—C16—H16	119.9
C4—C3—C2	118.46 (10)	O17—C17—O18	123.60 (12)
C4—C3—C9	120.74 (11)	O17—C17—C14	124.20 (13)
C2—C3—C9	120.79 (11)	O18—C17—C14	112.20 (11)
C3—C4—C4A	120.17 (11)	C17—O18—C18	115.32 (12)
C3—C4—H4	119.9	O18—C18—H18A	109.5

Table17 (continued).

C4A—C4—H4	119.9	O18—C18—H18B	109.5
C4—C4A—C5	121.60 (11)	H18A—C18—H18B	109.5
C4—C4A—C8A	119.55 (11)	O18—C18—H18C	109.5
C5—C4A—C8A	118.85 (11)	H18A—C18—H18C	109.5
C6—C5—C4A	120.34 (12)	H18B—C18—H18C	109.5
C6—C5—H5	119.8	F2—P1—F5	90.70 (5)
C4A—C5—H5	119.8	F2—P1—F4	90.89 (4)
C5—C6—C7	120.14 (12)	F5—P1—F4	89.92 (4)
C5—C6—H6	119.9	F2—P1—F3	90.27 (4)
C7—C6—H6	119.9	F5—P1—F3	89.88 (4)
C8—C7—C6	121.50 (12)	F4—P1—F3	178.83 (5)
C8—C7—H7	119.2	F2—P1—F6	90.16 (5)
C6—C7—H7	119.2	F5—P1—F6	179.14 (5)
C7—C8—C8A	118.97 (12)	F4—P1—F6	90.10 (4)
C7—C8—H8	120.5	F3—P1—F6	90.09 (4)
C8A—C8—H8	120.5	F2—P1—F1	179.16 (5)
N1—C8A—C8	121.65 (11)	F5—P1—F1	90.13 (5)
N1—C8A—C4A	118.17 (10)	F4—P1—F1	89.22 (4)
C8—C8A—C4A	120.18 (11)	F3—P1—F1	89.63 (4)
C10—C9—C3	174.29 (14)	F6—P1—F1	89.01 (4)
C9—C10—C11	176.92 (14)	N1A—C1A—C2A	178.4 (2)
C12—C11—C16	119.73 (11)	C1A—C2A—H2A1	109.5
C12—C11—C10	121.08 (12)	C1A—C2A—H2A2	109.5
C16—C11—C10	119.17 (11)	H2A1—C2A—H2A2	109.5
C13—C12—C11	119.76 (12)	C1A—C2A—H2A3	109.5
C13—C12—H12	120.1	H2A1—C2A—H2A3	109.5
C11—C12—H12	120.1	H2A2—C2A—H2A3	109.5

Table 18: Torsion angles (º) for **42aPF$_6$**

C8A—N1—C2—C3	-0.86 (17)	C5—C4A—C8A—N1	179.97 (10)
C1—N1—C2—C3	175.90 (10)	C4—C4A—C8A—C8	179.97 (11)
N1—C2—C3—C4	-0.08 (17)	C5—C4A—C8A—C8	-0.05 (17)
N1—C2—C3—C9	-178.71 (11)	C16—C11—C12—C13	-0.5 (2)
C2—C3—C4—C4A	0.95 (17)	C10—C11—C12—C13	178.38 (12)
C9—C3—C4—C4A	179.58 (11)	C11—C12—C13—C14	-0.2 (2)
C3—C4—C4A—C5	179.11 (11)	C12—C13—C14—C15	0.8 (2)
C3—C4—C4A—C8A	-0.90 (17)	C12—C13—C14—C17	-178.52 (13)
C4—C4A—C5—C6	-179.94 (12)	C13—C14—C15—C16	-0.7 (2)
C8A—C4A—C5—C6	0.07 (18)	C17—C14—C15—C16	178.58 (12)
C4A—C5—C6—C7	0.10 (19)	C14—C15—C16—C11	0.0 (2)
C5—C6—C7—C8	-0.3 (2)	C12—C11—C16—C15	0.6 (2)
C6—C7—C8—C8A	0.3 (2)	C10—C11—C16—C15	-178.32 (12)
C2—N1—C8A—C8	-179.09 (11)	C13—C14—C17—O17	2.8 (2)
C1—N1—C8A—C8	4.20 (16)	C15—C14—C17—O17	-176.42 (14)

Table18 (continued).

C2—N1—C8A—C4A	0.89 (16)	C13—C14—C17—O18	-177.77 (12)
C1—N1—C8A—C4A	-175.82 (10)	C15—C14—C17—O18	2.97 (18)
C7—C8—C8A—N1	179.82 (11)	O17—C17—O18—C18	-0.8 (2)
C7—C8—C8A—C4A	-0.16 (18)	C14—C17—O18—C18	179.77 (13)
C4—C4A—C8A—N1	-0.01 (16)		

Table 19: Hydrogen-bond geometry (Å, º) for **42aPF$_6$**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···F2	0.98	2.61	3.3969 (15)	137
C1—H1*C*···F1^{i}	0.98	2.44	3.2638 (15)	142
C1—H1*C*···F5^{i}	0.98	2.60	3.5290 (15)	158
C2—H2···F1^{ii}	0.95	2.56	3.4874 (14)	165
C2—H2···F4^{ii}	0.95	2.45	3.2002 (14)	135
C8—H8···F5^{i}	0.95	2.58	3.2060 (15)	124
C18—H18*A*···F4^{iii}	0.98	2.61	3.3911 (19)	136
C18—H18*B*···F2^{iii}	0.98	2.55	3.1021 (17)	116
C2*A*—H2*A*1···F5^{ii}	0.98	2.58	3.414 (2)	143
C2*A*—H2*A*2···N1*A*^{iv}	0.98	2.61	3.533 (3)	157
C2*A*—H2*A*3···O17^{iv}	0.98	2.31	3.279 (2)	168

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) -*x*+1, *y*-1/2, -*z*+1/2; (iii) *x*+1, -*y*+3/2, *z*+1/2; (iv) -*x*+2, *y*-1/2, -*z*+1/2.

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Crystal structure determination of 3-((2-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolin-1-ium hexafluorophosphate 43PF$_6$

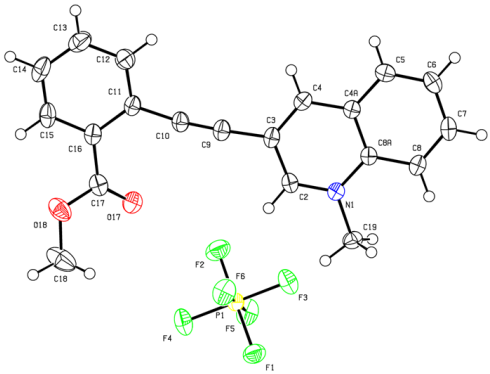

Figure 38: X-ray structure of molecules **43PF$_6$**

Table 20: Crystallography data for **43PF$_6$**

$C_{20}H_{16}NO_2 \cdot F_6P$	$F(000)$ = 912
M_r = 447.31	D_x = 1.570 Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 13.8445 (5) Å	Cell parameters from 9904 reflections
b = 8.2667 (3) Å	θ = 3.6–72.1°
c = 17.2086 (6) Å	μ = 2.00 mm^{-1}
β = 106.117 (1)°	T = 123 K
V = 1892.09 (12) Å^3	Plates, yellow
Z = 4	0.20 × 0.18 × 0.03 mm

Table 21: Data collection for **43PF$_6$**

Bruker D8 VENTURE diffractometer with Photon100 detector	3717 independent reflections
Radiation source: INCOATEC microfocus sealed tube	3370 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	R_{int} = 0.029
rotation in ϕ and ω, 0.5°, shutterless scans	θ_{max} = 72.1°, θ_{min} = 3.6°

Table 21 (continued).

Absorption correction: multi-scan *SADABS* V2014/5 (Bruker AXS Inc.)	h = -16→17
T_{min} = 0.806, T_{max} = 0.942	k = -10→10
28286 measured reflections	l = -21→18

Table 22: Refinement for **43PF$_6$**

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.033	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.089	H-atom parameters constrained
S = 1.06	$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.822P]$ where $P = (F_o^2 + 2F_c^2)/3$
3717 reflections	$(\Delta/\sigma)_{max} < 0.001$
273 parameters	$\Delta\rangle_{max}$ = 0.31 e Å^{-3}
0 restraints	$\Delta\rangle_{min}$ = -0.26 e Å^{-3}

Computing details

Data collection: *APEX3* v2015.9-RC2 (Bruker AXS); cell refinement: *APEX3* v2015.9-RC2 (Bruker AXS); data reduction: *SAINT* V8.35A (Bruker AXS Inc., 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 0.5 deg., 18+1 runs, 4751 frames, 10/20 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by

crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes

Table 23: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **43PF$_6$**

	X	*y*	*z*	U_{iso}*/U_{eq}
N1	0.33004 (9)	0.79915 (14)	0.41179 (7)	0.0226 (2)
C2	0.39323 (11)	0.71094 (17)	0.38421 (9)	0.0245 (3)
H2	0.3713	0.6678	0.3310	0.029*
C3	0.49205 (11)	0.67925 (17)	0.43147 (9)	0.0248 (3)
C4	0.52229 (11)	0.73898 (17)	0.50900 (9)	0.0249 (3)
H4	0.5883	0.7172	0.5421	0.030*
C4A	0.45629 (10)	0.83190 (17)	0.53964 (8)	0.0223 (3)
C5	0.48436 (11)	0.89568 (19)	0.61923 (9)	0.0277 (3)
H5	0.5497	0.8750	0.6539	0.033*
C6	0.41819 (12)	0.98660 (19)	0.64643 (9)	0.0309 (3)
H6	0.4375	1.0288	0.6999	0.037*
C7	0.32159 (12)	1.01797 (19)	0.59563 (10)	0.0314 (3)
H7	0.2765	1.0820	0.6153	0.038*
C8	0.29083 (11)	0.95825 (18)	0.51825 (9)	0.0271 (3)
H8	0.2251	0.9805	0.4847	0.033*
C8A	0.35780 (10)	0.86380 (16)	0.48934 (8)	0.0216 (3)
C9	0.55845 (11)	0.58698 (19)	0.39828 (9)	0.0282 (3)
C10	0.61746 (11)	0.51105 (18)	0.37427 (9)	0.0271 (3)
C11	0.69810 (11)	0.42547 (18)	0.35513 (9)	0.0259 (3)
C12	0.79299 (12)	0.4314 (2)	0.41142 (10)	0.0345 (4)
H12	0.8013	0.4880	0.4609	0.041*
C13	0.87471 (13)	0.3558 (2)	0.39596 (11)	0.0412 (4)
H13	0.9390	0.3630	0.4342	0.049*
C14	0.86346 (14)	0.2699 (2)	0.32530 (12)	0.0408 (4)
H14	0.9192	0.2142	0.3159	0.049*
C15	0.77152 (13)	0.2652 (2)	0.26858 (10)	0.0342 (4)
H15	0.7646	0.2074	0.2196	0.041*
C16	0.68794 (12)	0.34390 (17)	0.28153 (9)	0.0267 (3)
C17	0.59099 (12)	0.34481 (18)	0.21692 (10)	0.0298 (3)
O17	0.50870 (9)	0.36330 (15)	0.22584 (7)	0.0382 (3)
O18	0.60762 (9)	0.32415 (17)	0.14411 (7)	0.0427 (3)
C18	0.51905 (16)	0.3236 (3)	0.07651 (11)	0.0564 (6)
H18A	0.4770	0.2305	0.0807	0.085*
H18B	0.5386	0.3164	0.0261	0.085*
H18C	0.4811	0.4237	0.0766	0.085*
C19	0.22672 (11)	0.8250 (2)	0.35912 (9)	0.0294 (3)
H19A	0.2193	0.7716	0.3069	0.044*
H19B	0.2143	0.9412	0.3505	0.044*

Table 23 (continued).

	x	*Y*	*z*	U_{iso}*/U_{eq}
H19C	0.1782	0.7792	0.3851	0.044*
P1	0.33194 (3)	0.85428 (4)	0.14833 (2)	0.02443 (11)
F1	0.24606 (7)	0.95578 (12)	0.08596 (6)	0.0387 (2)
F2	0.41610 (8)	0.75282 (14)	0.21148 (6)	0.0455 (3)
F3	0.31331 (8)	0.95872 (13)	0.22116 (6)	0.0425 (3)
F4	0.35093 (9)	0.75036 (13)	0.07591 (6)	0.0445 (3)
F5	0.24885 (7)	0.72686 (12)	0.15829 (7)	0.0409 (2)
F6	0.41371 (7)	0.98195 (13)	0.13813 (7)	0.0422 (3)

Table 24: Atomic displacement parameters (Å^2) for **43PF$_6$**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0230 (6)	0.0193 (6)	0.0263 (6)	-0.0017 (5)	0.0084 (5)	0.0018 (5)
C2	0.0314 (7)	0.0195 (7)	0.0260 (7)	-0.0024 (6)	0.0137 (6)	-0.0001 (5)
C3	0.0279 (7)	0.0193 (7)	0.0322 (8)	0.0003 (6)	0.0168 (6)	0.0038 (6)
C4	0.0237 (7)	0.0220 (7)	0.0309 (7)	0.0004 (5)	0.0106 (6)	0.0064 (6)
C4A	0.0251 (7)	0.0188 (7)	0.0252 (7)	-0.0015 (5)	0.0107 (5)	0.0043 (5)
C5	0.0303 (7)	0.0261 (7)	0.0261 (7)	-0.0042 (6)	0.0071 (6)	0.0034 (6)
C6	0.0406 (9)	0.0285 (8)	0.0268 (8)	-0.0066 (7)	0.0149 (6)	-0.0032 (6)
C7	0.0377 (8)	0.0252 (7)	0.0379 (9)	-0.0003 (6)	0.0214 (7)	-0.0038 (6)
C8	0.0256 (7)	0.0230 (7)	0.0354 (8)	0.0008 (6)	0.0129 (6)	0.0008 (6)
C8A	0.0246 (7)	0.0175 (6)	0.0252 (7)	-0.0026 (5)	0.0108 (5)	0.0021 (5)
C9	0.0315 (8)	0.0243 (7)	0.0333 (8)	0.0004 (6)	0.0163 (6)	0.0029 (6)
C10	0.0312 (8)	0.0248 (7)	0.0293 (8)	0.0000 (6)	0.0148 (6)	0.0026 (6)
C11	0.0288 (7)	0.0229 (7)	0.0309 (7)	0.0023 (6)	0.0161 (6)	0.0056 (6)
C12	0.0353 (8)	0.0390 (9)	0.0315 (8)	0.0015 (7)	0.0132 (7)	0.0036 (7)
C13	0.0292 (8)	0.0514 (11)	0.0442 (10)	0.0074 (8)	0.0120 (7)	0.0130 (8)
C14	0.0379 (9)	0.0393 (10)	0.0543 (11)	0.0140 (7)	0.0279 (8)	0.0140 (8)
C15	0.0450 (9)	0.0254 (8)	0.0417 (9)	0.0044 (7)	0.0278 (8)	0.0035 (6)
C16	0.0323 (8)	0.0204 (7)	0.0324 (8)	-0.0001 (6)	0.0173 (6)	0.0043 (6)
C17	0.0380 (8)	0.0237 (7)	0.0316 (8)	-0.0043 (6)	0.0160 (7)	0.0001 (6)
O17	0.0317 (6)	0.0454 (7)	0.0393 (7)	0.0026 (5)	0.0130 (5)	-0.0010 (5)
O18	0.0417 (7)	0.0589 (8)	0.0313 (6)	-0.0150 (6)	0.0165 (5)	-0.0071 (6)
C18	0.0527 (12)	0.0848 (16)	0.0324 (10)	-0.0298 (11)	0.0128 (8)	-0.0049 (10)
C19	0.0249 (7)	0.0292 (8)	0.0314 (8)	-0.0002 (6)	0.0034 (6)	-0.0002 (6)
P1	0.02498 (19)	0.0239 (2)	0.0257 (2)	-0.00095 (14)	0.00906 (14)	0.00023 (14)
F1	0.0359 (5)	0.0399 (6)	0.0372 (5)	0.0062 (4)	0.0053 (4)	0.0060 (4)
F2	0.0373 (5)	0.0538 (7)	0.0447 (6)	0.0108 (5)	0.0102 (4)	0.0162 (5)
F3	0.0574 (6)	0.0403 (6)	0.0344 (5)	-0.0020 (5)	0.0203 (5)	-0.0075 (4)
F4	0.0601 (7)	0.0387 (6)	0.0418 (6)	0.0018 (5)	0.0260 (5)	-0.0091 (4)
F5	0.0380 (5)	0.0306 (5)	0.0594 (6)	-0.0073 (4)	0.0223 (5)	0.0005 (4)
F6	0.0366 (5)	0.0370 (5)	0.0575 (6)	-0.0082 (4)	0.0204 (5)	0.0028 (5)

Table 25: Bond lengths (Å) for **43PF$_6$**

N1—C2	1.3240 (19)	C12—H12	0.9500
N1—C8A	1.3892 (18)	C13—C14	1.379 (3)
N1—C19	1.4810 (18)	C13—H13	0.9500
C2—C3	1.409 (2)	C14—C15	1.373 (3)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.374 (2)	C15—C16	1.398 (2)
C3—C9	1.430 (2)	C15—H15	0.9500
C4—C4A	1.404 (2)	C16—C17	1.486 (2)
C4—H4	0.9500	C17—O17	1.201 (2)
C4A—C5	1.418 (2)	C17—O18	1.3463 (19)
C4A—C8A	1.422 (2)	O18—C18	1.437 (2)
C5—C6	1.364 (2)	C18—H18A	0.9800
C5—H5	0.9500	C18—H18B	0.9800
C6—C7	1.404 (2)	C18—H18C	0.9800
C6—H6	0.9500	C19—H19A	0.9800
C7—C8	1.372 (2)	C19—H19B	0.9800
C7—H7	0.9500	C19—H19C	0.9800
C8—C8A	1.405 (2)	P1—F6	1.5927 (10)
C8—H8	0.9500	P1—F2	1.5935 (10)
C9—C10	1.191 (2)	P1—F4	1.5944 (10)
C10—C11	1.435 (2)	P1—F1	1.6003 (10)
C11—C12	1.400 (2)	P1—F3	1.6007 (10)
C11—C16	1.407 (2)	P1—F5	1.6037 (10)
C12—C13	1.381 (2)		

Table 26: Bond angles (°) for **43PF$_6$**

C2—N1—C8A	121.48 (12)	C15—C14—C13	119.81 (15)
C2—N1—C19	118.82 (12)	C15—C14—H14	120.1
C8A—N1—C19	119.68 (12)	C13—C14—H14	120.1
N1—C2—C3	121.87 (13)	C14—C15—C16	121.22 (16)
N1—C2—H2	119.1	C14—C15—H15	119.4
C3—C2—H2	119.1	C16—C15—H15	119.4
C4—C3—C2	118.62 (13)	C15—C16—C11	119.09 (15)
C4—C3—C9	121.54 (14)	C15—C16—C17	119.90 (14)
C2—C3—C9	119.84 (14)	C11—C16—C17	120.98 (13)
C3—C4—C4A	120.44 (13)	O17—C17—O18	123.27 (15)
C3—C4—H4	119.8	O17—C17—C16	126.65 (14)
C4A—C4—H4	119.8	O18—C17—C16	110.08 (13)
C4—C4A—C5	122.28 (14)	C17—O18—C18	115.20 (14)
C4—C4A—C8A	119.14 (13)	O18—C18—H18A	109.5
C5—C4A—C8A	118.58 (13)	O18—C18—H18B	109.5
C6—C5—C4A	120.42 (14)	H18A—C18—H18B	109.5
C6—C5—H5	119.8	O18—C18—H18C	109.5
C4A—C5—H5	119.8	H18A—C18—H18C	109.5
C5—C6—C7	120.16 (14)	H18B—C18—H18C	109.5
C5—C6—H6	119.9	N1—C19—H19A	109.5
C7—C6—H6	119.9	N1—C19—H19B	109.5

Table 26 (continued).

C8—C7—C6	121.54 (14)	H19A—C19—H19B	109.5
C8—C7—H7	119.2	N1—C19—H19C	109.5
C6—C7—H7	119.2	H19A—C19—H19C	109.5
C7—C8—C8A	119.08 (14)	H19B—C19—H19C	109.5
C7—C8—H8	120.5	F6—P1—F2	90.94 (6)
C8A—C8—H8	120.5	F6—P1—F4	89.68 (6)
N1—C8A—C8	121.35 (13)	F2—P1—F4	90.09 (6)
N1—C8A—C4A	118.44 (12)	F6—P1—F1	89.83 (6)
C8—C8A—C4A	120.21 (13)	F2—P1—F1	178.94 (6)
C10—C9—C3	176.66 (18)	F4—P1—F1	90.65 (6)
C9—C10—C11	172.44 (17)	F6—P1—F3	90.16 (6)
C12—C11—C16	118.66 (14)	F2—P1—F3	89.78 (6)
C12—C11—C10	117.67 (14)	F4—P1—F3	179.79 (7)
C16—C11—C10	123.58 (14)	F1—P1—F3	89.49 (6)
C13—C12—C11	120.83 (16)	F6—P1—F5	179.50 (6)
C13—C12—H12	119.6	F2—P1—F5	89.53 (6)
C11—C12—H12	119.6	F4—P1—F5	90.49 (6)
C14—C13—C12	120.30 (17)	F1—P1—F5	89.69 (6)
C14—C13—H13	119.8	F3—P1—F5	89.67 (6)
C12—C13—H13	119.8		

Table 27: Torsion angles (º) for **43PF$_6$**

C8A—N1—C2—C3	-0.7 (2)	C5—C4A—C8A—N1	-179.08 (12)
C19—N1—C2—C3	-178.96 (13)	C4—C4A—C8A—C8	-179.16 (13)
N1—C2—C3—C4	1.5 (2)	C5—C4A—C8A—C8	0.7 (2)
N1—C2—C3—C9	-178.31 (13)	C16—C11—C12—C13	-1.4 (2)
C2—C3—C4—C4A	-1.1 (2)	C10—C11—C12—C13	-178.09 (15)
C9—C3—C4—C4A	178.76 (13)	C11—C12—C13—C14	-1.5 (3)
C3—C4—C4A—C5	179.94 (13)	C12—C13—C14—C15	2.7 (3)
C3—C4—C4A—C8A	-0.2 (2)	C13—C14—C15—C16	-1.1 (3)
C4—C4A—C5—C6	179.43 (14)	C14—C15—C16—C11	-1.8 (2)
C8A—C4A—C5—C6	-0.5 (2)	C14—C15—C16—C17	176.33 (15)
C4A—C5—C6—C7	-0.1 (2)	C12—C11—C16—C15	3.0 (2)
C5—C6—C7—C8	0.4 (2)	C10—C11—C16—C15	179.48 (14)
C6—C7—C8—C8A	-0.1 (2)	C12—C11—C16—C17	-175.13 (14)
C2—N1—C8A—C8	179.56 (13)	C10—C11—C16—C17	1.4 (2)
C19—N1—C8A—C8	-2.2 (2)	C15—C16—C17—O17	156.64 (16)
C2—N1—C8A—C4A	-0.63 (19)	C11—C16—C17—O17	-25.3 (2)
C19—N1—C8A—C4A	177.66 (12)	C15—C16—C17—O18	-24.4 (2)
C7—C8—C8A—N1	179.35 (13)	C11—C16—C17—O18	153.67 (14)
C7—C8—C8A—C4A	-0.5 (2)	O17—C17—O18—C18	-0.7 (3)
C4—C4A—C8A—N1	1.03 (19)	C16—C17—O18—C18	-179.73 (16)

Table 28: Hydrogen-bond geometry (Å, º) for **43PF$_6$**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···F2	0.95	2.41	3.0947 (18)	129
C8—H8···F4^{i}	0.95	2.56	3.2470 (19)	129
C18—H18*A*···F6^{ii}	0.98	2.54	3.477 (2)	160
C19—H19*B*···F5^{i}	0.98	2.43	3.3611 (19)	159

Symmetry codes: (i) -*x*+1/2, *y*+1/2, -*z*+1/2; (ii) *x*, *y*-1, *z*.

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Crystal structure determination of 3-((2-((methoxy-d3)carbonyl)-phenyl)ethynyl)-1-methylquinolin-1-ium hexafluorophosphate 48PF$_6$

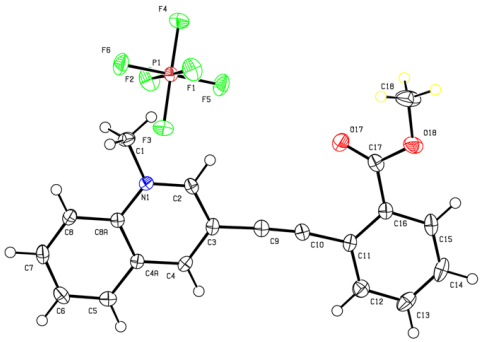

Figure 39: X-ray structure of molecules **48PF$_6$**

Table 29: Crystallography data for **48PF$_6$**

$C_{20}H_{13}D_3NO_2 \cdot F_6P$	$F(000)$ = 912
M_r = 450.33	D_x = 1.584 Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 13.8271 (8) Å	Cell parameters from 9979 reflections
b = 8.2406 (5) Å	θ = 2.5–27.5°
c = 17.2704 (9) Å	μ = 0.22 mm^{-1}
β = 106.370 (2)°	T = 123 K
V = 1888.08 (19) Å^3	Plates, colourless
Z = 4	0.36 × 0.26 × 0.08 mm

Table 30: Data collection for **48PF$_6$**

Bruker D8 VENTURE diffractometer with Photon100 detector	4338 independent reflections
Radiation source: INCOATEC microfocus sealed tube	3479 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	R_{int} = 0.040
rotation in ϕ and ω, 1°, shutterless scans	θ_{max} = 27.5°, θ_{min} = 2.2°
Absorption correction: multi-scan *SADABS* (Sheldrick, 2014)	h = -17→17
T_{min} = 0.924, T_{max} = 0.987	k = -10→10
29589 measured reflections	l = -22→21

Table 31: Refinement for **48PF$_6$**

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.2976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
4338 reflections	$\Delta\rangle_{max} = 0.28$ e Å^{-3}
274 parameters	$\Delta\rangle_{min} = -0.28$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0044 (6)

Computing details

Data collection: *APEX3*; cell refinement: *APEX3*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 1 deg., 4+1 runs, 640 frames, 15 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. CD_3: due to reesterefication in MeOD during the reaction.

Table 32: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **48PF$_6$**

	x	*Y*	*Z*	U_{iso}*/U_{eq}
C1	0.77388 (11)	0.8267 (2)	0.14128 (10)	0.0221 (4)
H1A	0.7811	0.7738	0.1934	0.033*
H1B	0.7864	0.9433	0.1496	0.033*
H1C	0.8227	0.7802	0.1159	0.033*
N1	0.67031 (9)	0.80046 (16)	0.08822 (8)	0.0158 (3)
C2	0.60693 (12)	0.71244 (19)	0.11574 (9)	0.0176 (3)
H2	0.6289	0.6700	0.1690	0.021*
C3	0.50806 (12)	0.68007 (19)	0.06833 (10)	0.0176 (3)
C4	0.47789 (11)	0.73933 (19)	-0.00929 (9)	0.0172 (3)
H4	0.4117	0.7175	-0.0425	0.021*
C4A	0.54436 (11)	0.83211 (18)	-0.03982 (9)	0.0155 (3)
C5	0.51604 (12)	0.8950 (2)	-0.11938 (9)	0.0198 (3)
H5	0.4505	0.8739	-0.1540	0.024*
C6	0.58245 (13)	0.9857 (2)	-0.14660 (10)	0.0232 (4)
H6	0.5631	1.0274	-0.2000	0.028*
C7	0.67942 (13)	1.0173 (2)	-0.09559 (10)	0.0237 (4)
H7	0.7248	1.0809	-0.1152	0.028*
C8	0.71005 (12)	0.9585 (2)	-0.01818 (10)	0.0200 (3)
H8	0.7758	0.9811	0.0155	0.024*
C8A	0.64272 (11)	0.86425 (18)	0.01052 (9)	0.0152 (3)
C9	0.44153 (12)	0.5884 (2)	0.10145 (10)	0.0207 (3)
C10	0.38222 (12)	0.5121 (2)	0.12555 (9)	0.0192 (3)
C11	0.30138 (11)	0.42706 (19)	0.14469 (9)	0.0178 (3)
C12	0.20626 (13)	0.4337 (2)	0.08815 (10)	0.0251 (4)
H12	0.1979	0.4908	0.0389	0.030*
C13	0.12439 (13)	0.3577 (2)	0.10352 (11)	0.0307 (4)
H13	0.0600	0.3648	0.0652	0.037*
C14	0.13529 (14)	0.2719 (2)	0.17396 (12)	0.0304 (4)
H14	0.0792	0.2168	0.1832	0.036*
C15	0.22805 (13)	0.2664 (2)	0.23103 (11)	0.0251 (4)
H15	0.2352	0.2084	0.2799	0.030*
C16	0.31178 (12)	0.3451 (2)	0.21796 (9)	0.0184 (3)
C17	0.40885 (13)	0.3459 (2)	0.28259 (10)	0.0218 (3)
O17	0.49106 (9)	0.36414 (16)	0.27384 (7)	0.0298 (3)
O18	0.39197 (9)	0.32493 (17)	0.35513 (7)	0.0323 (3)
C18	0.48093 (16)	0.3239 (3)	0.42299 (11)	0.0436 (6)
D18A	0.5224	0.2293	0.4194	0.065*
D18B	0.4612	0.3185	0.4732	0.065*
D18C	0.5197	0.4233	0.4226	0.065*
P1	0.83181 (3)	0.35543 (5)	0.14860 (2)	0.01794 (11)
F1	0.81239 (8)	0.46015 (14)	0.22074 (6)	0.0340 (3)
F2	0.85154 (9)	0.25105 (14)	0.07658 (6)	0.0359 (3)
F3	0.74647 (7)	0.45740 (13)	0.08549 (6)	0.0312 (3)
F4	0.91568 (8)	0.25295 (15)	0.21193 (7)	0.0365 (3)
F5	0.74791 (8)	0.22794 (13)	0.15746 (7)	0.0333 (3)
F6	0.91446 (8)	0.48316 (13)	0.13943 (7)	0.0338 (3)

Table 33: Atomic displacement parameters (Å^2) for **48PF$_6$**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0176 (8)	0.0218 (9)	0.0240 (8)	-0.0007 (6)	0.0007 (6)	-0.0005 (7)
N1	0.0159 (6)	0.0132 (6)	0.0183 (6)	0.0007 (5)	0.0046 (5)	-0.0016 (5)
C2	0.0237 (8)	0.0130 (8)	0.0186 (7)	0.0025 (6)	0.0098 (6)	0.0004 (6)
C3	0.0205 (8)	0.0121 (8)	0.0236 (8)	-0.0005 (6)	0.0117 (6)	-0.0026 (6)
C4	0.0153 (7)	0.0150 (8)	0.0220 (8)	-0.0011 (6)	0.0063 (6)	-0.0051 (6)
C4A	0.0176 (7)	0.0115 (7)	0.0188 (7)	0.0012 (6)	0.0074 (6)	-0.0024 (6)
C5	0.0213 (8)	0.0179 (8)	0.0191 (8)	0.0029 (6)	0.0042 (6)	-0.0036 (6)
C6	0.0319 (9)	0.0197 (9)	0.0206 (8)	0.0047 (7)	0.0114 (7)	0.0035 (7)
C7	0.0271 (9)	0.0190 (8)	0.0302 (9)	-0.0010 (7)	0.0168 (7)	0.0029 (7)
C8	0.0172 (7)	0.0166 (8)	0.0278 (8)	-0.0001 (6)	0.0086 (6)	0.0002 (7)
C8A	0.0180 (7)	0.0112 (7)	0.0181 (7)	0.0019 (6)	0.0077 (6)	-0.0022 (6)
C9	0.0234 (8)	0.0171 (8)	0.0232 (8)	0.0001 (7)	0.0094 (7)	-0.0022 (7)
C10	0.0236 (8)	0.0163 (8)	0.0193 (8)	-0.0003 (6)	0.0088 (6)	-0.0025 (6)
C11	0.0202 (8)	0.0142 (8)	0.0219 (8)	-0.0021 (6)	0.0105 (6)	-0.0048 (6)
C12	0.0262 (9)	0.0284 (10)	0.0219 (8)	-0.0005 (7)	0.0086 (7)	-0.0032 (7)
C13	0.0200 (8)	0.0384 (11)	0.0329 (10)	-0.0052 (8)	0.0061 (7)	-0.0118 (9)
C14	0.0272 (9)	0.0290 (10)	0.0414 (11)	-0.0117 (8)	0.0203 (8)	-0.0115 (8)
C15	0.0343 (10)	0.0173 (8)	0.0307 (9)	-0.0036 (7)	0.0206 (8)	-0.0023 (7)
C16	0.0221 (8)	0.0139 (8)	0.0218 (8)	0.0011 (6)	0.0107 (6)	-0.0031 (6)
C17	0.0290 (9)	0.0160 (8)	0.0229 (8)	0.0033 (7)	0.0114 (7)	-0.0003 (7)
O17	0.0231 (6)	0.0371 (8)	0.0300 (7)	-0.0022 (5)	0.0088 (5)	0.0012 (6)
O18	0.0315 (7)	0.0461 (8)	0.0209 (6)	0.0115 (6)	0.0101 (5)	0.0049 (6)
C18	0.0404 (11)	0.0669 (16)	0.0219 (9)	0.0241 (11)	0.0059 (8)	0.0034 (10)
P1	0.0185 (2)	0.0171 (2)	0.0186 (2)	-0.00068 (16)	0.00583 (15)	0.00030 (16)
F1	0.0464 (6)	0.0332 (6)	0.0264 (5)	-0.0002 (5)	0.0169 (5)	-0.0073 (5)
F2	0.0509 (7)	0.0299 (6)	0.0322 (6)	0.0021 (5)	0.0207 (5)	-0.0083 (5)
F3	0.0284 (5)	0.0323 (6)	0.0292 (5)	0.0066 (5)	0.0021 (4)	0.0065 (5)
F4	0.0288 (6)	0.0438 (7)	0.0354 (6)	0.0105 (5)	0.0066 (5)	0.0159 (5)
F5	0.0282 (5)	0.0238 (6)	0.0514 (7)	-0.0067 (4)	0.0169 (5)	0.0017 (5)
F6	0.0283 (5)	0.0288 (6)	0.0478 (7)	-0.0088 (5)	0.0164 (5)	0.0022 (5)

Table 34: Bond lengths (Å) for **48PF$_6$**

C1—N1	1.4824 (19)	C11—C12	1.401 (2)
C1—H1A	0.9800	C11—C16	1.406 (2)
C1—H1B	0.9800	C12—C13	1.383 (2)
C1—H1C	0.9800	C12—H12	0.9500
N1—C2	1.325 (2)	C13—C14	1.378 (3)
N1—C8A	1.3907 (19)	C13—H13	0.9500
C2—C3	1.407 (2)	C14—C15	1.381 (3)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.376 (2)	C15—C16	1.400 (2)
C3—C9	1.429 (2)	C15—H15	0.9500
C4—C4A	1.407 (2)	C16—C17	1.484 (2)
C4—H4	0.9500	C17—O17	1.198 (2)

Table 34 (continued).

C4A—C5	1.417 (2)	C17—O18	1.348 (2)
C4A—C8A	1.417 (2)	O18—C18	1.440 (2)
C5—C6	1.366 (2)	C18—D18A	0.9800
C5—H5	0.9500	C18—D18B	0.9800
C6—C7	1.406 (2)	C18—D18C	0.9800
C6—H6	0.9500	P1—F4	1.5935 (11)
C7—C8	1.372 (2)	P1—F6	1.5940 (11)
C7—H7	0.9500	P1—F2	1.5976 (11)
C8—C8A	1.406 (2)	P1—F1	1.5993 (11)
C8—H8	0.9500	P1—F3	1.6005 (10)
C9—C10	1.198 (2)	P1—F5	1.6040 (11)
C10—C11	1.434 (2)		

Table 35: Bond angles (º) for **48PF$_6$**

N1—C1—H1A	109.5	C13—C12—C11	120.45 (16)
N1—C1—H1B	109.5	C13—C12—H12	119.8
H1A—C1—H1B	109.5	C11—C12—H12	119.8
N1—C1—H1C	109.5	C14—C13—C12	120.66 (17)
H1A—C1—H1C	109.5	C14—C13—H13	119.7
H1B—C1—H1C	109.5	C12—C13—H13	119.7
C2—N1—C8A	121.59 (13)	C13—C14—C15	119.70 (16)
C2—N1—C1	118.66 (13)	C13—C14—H14	120.1
C8A—N1—C1	119.73 (13)	C15—C14—H14	120.1
N1—C2—C3	121.84 (14)	C14—C15—C16	120.92 (16)
N1—C2—H2	119.1	C14—C15—H15	119.5
C3—C2—H2	119.1	C16—C15—H15	119.5
C4—C3—C2	118.53 (14)	C15—C16—C11	119.23 (15)
C4—C3—C9	121.67 (15)	C15—C16—C17	119.64 (15)
C2—C3—C9	119.80 (15)	C11—C16—C17	121.08 (14)
C3—C4—C4A	120.46 (14)	O17—C17—O18	123.52 (16)
C3—C4—H4	119.8	O17—C17—C16	126.51 (15)
C4A—C4—H4	119.8	O18—C17—C16	109.96 (14)
C4—C4A—C5	122.07 (14)	C17—O18—C18	115.15 (14)
C4—C4A—C8A	119.13 (14)	O18—C18—D18A	109.5
C5—C4A—C8A	118.80 (14)	O18—C18—D18B	109.5
C6—C5—C4A	120.33 (15)	D18A—C18—D18B	109.5
C6—C5—H5	119.8	O18—C18—D18C	109.5
C4A—C5—H5	119.8	D18A—C18—D18C	109.5
C5—C6—C7	120.06 (15)	D18B—C18—D18C	109.5
C5—C6—H6	120.0	F4—P1—F6	90.84 (6)
C7—C6—H6	120.0	F4—P1—F2	89.90 (6)
C8—C7—C6	121.53 (15)	F6—P1—F2	89.64 (6)
C8—C7—H7	119.2	F4—P1—F1	90.04 (6)
C6—C7—H7	119.2	F6—P1—F1	90.20 (6)
C7—C8—C8A	119.05 (15)	F2—P1—F1	179.83 (7)
C7—C8—H8	120.5	F4—P1—F3	179.25 (6)

Table 35 (continued).

C8A—C8—H8	120.5	F6—P1—F3	89.84 (6)
N1—C8A—C8	121.35 (14)	F2—P1—F3	90.42 (6)
N1—C8A—C4A	118.43 (13)	F1—P1—F3	89.64 (6)
C8—C8A—C4A	120.23 (14)	F4—P1—F5	89.62 (6)
C10—C9—C3	176.73 (18)	F6—P1—F5	179.52 (7)
C9—C10—C11	172.35 (17)	F2—P1—F5	90.49 (6)
C12—C11—C16	118.96 (14)	F1—P1—F5	89.67 (6)
C12—C11—C10	117.37 (15)	F3—P1—F5	89.69 (6)
C16—C11—C10	123.61 (14)		

Table 36: Torsion angles (º) for **48PF$_6$**

C8A—N1—C2—C3	-0.7 (2)	C5—C4A—C8A—N1	-179.25 (14)
C1—N1—C2—C3	-178.88 (14)	C4—C4A—C8A—C8	-179.12 (14)
N1—C2—C3—C4	1.4 (2)	C5—C4A—C8A—C8	0.7 (2)
N1—C2—C3—C9	-178.21 (14)	C16—C11—C12—C13	-1.4 (2)
C2—C3—C4—C4A	-0.9 (2)	C10—C11—C12—C13	-178.47 (16)
C9—C3—C4—C4A	178.69 (14)	C11—C12—C13—C14	-1.2 (3)
C3—C4—C4A—C5	179.94 (15)	C12—C13—C14—C15	2.3 (3)
C3—C4—C4A—C8A	-0.2 (2)	C13—C14—C15—C16	-0.9 (3)
C4—C4A—C5—C6	179.45 (15)	C14—C15—C16—C11	-1.7 (2)
C8A—C4A—C5—C6	-0.4 (2)	C14—C15—C16—C17	176.08 (16)
C4A—C5—C6—C7	-0.1 (2)	C12—C11—C16—C15	2.8 (2)
C5—C6—C7—C8	0.2 (3)	C10—C11—C16—C15	179.65 (15)
C6—C7—C8—C8A	0.1 (2)	C12—C11—C16—C17	-174.96 (15)
C2—N1—C8A—C8	179.57 (14)	C10—C11—C16—C17	1.9 (2)
C1—N1—C8A—C8	-2.3 (2)	C15—C16—C17—O17	156.77 (17)
C2—N1—C8A—C4A	-0.5 (2)	C11—C16—C17—O17	-25.5 (3)
C1—N1—C8A—C4A	177.71 (14)	C15—C16—C17—O18	-24.1 (2)
C7—C8—C8A—N1	179.40 (15)	C11—C16—C17—O18	153.60 (15)
C7—C8—C8A—C4A	-0.6 (2)	O17—C17—O18—C18	-0.7 (3)
C4—C4A—C8A—N1	0.9 (2)	C16—C17—O18—C18	-179.86 (16)

Table 37: Hydrogen-bond geometry (Å, º) for **48PF$_6$**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···F5^{i}	0.98	2.42	3.346 (2)	158
C2—H2···F4^{ii}	0.95	2.41	3.0971 (19)	129
C8—H8···F2^{i}	0.95	2.56	3.242 (2)	129
C18—D18*A*···F6^{iii}	0.98	2.53	3.467 (2)	160

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) -*x*+3/2, *y*+1/2, -*z*+1/2; (iii) -*x*+3/2, *y*-1/2, -*z*+1/2.

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Crystal structure determination of 1-methyl-3-(naphthalen-1-yl)quinoline-2(1H)-thione 95b

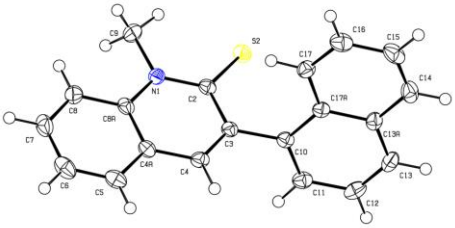


Figure 40: X-ray structure of molecules **95b**

Table 38: Crystallography data for **95b**

$C_{20}H_{15}NS$	D_x = 1.349 Mg m^{-3}
M_r = 301.39	Cu $K\alpha$ radiation, λ = 1.54178 Å
Orthorhombic, $P2_12_12_1$ (no.19)	Cell parameters from 9772 reflections
a = 8.3590 (5) Å	θ = 3.2–72.1°
b = 12.9270 (7) Å	μ = 1.87 mm^{-1}
c = 13.7331 (7) Å	T = 123 K
V = 1483.95 (14) Å^3	Blocks, yellow
Z = 4	0.20 × 0.18 × 0.10 mm
F(000) = 632	

Table 39: Data collection for **95b**

Bruker D8 VENTURE diffractometer with Photon100 detector	2906 independent reflections
Radiation source: INCOATEC microfocus sealed tube	2872 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	R_{int} = 0.021
rotation in ϕ and ω, 1°, shutterless scans	θ_{max} = 72.2°, θ_{min} = 4.7°
Absorption correction: multi-scan	h = -9→10
SADABS (Sheldrick, 2014)	
T_{min} = 0.798, T_{max} = 0.864	k = -12→15
10197 measured reflections	l = -16→16

Table 40: Refinement for **95b**

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.026$	H-atom parameters constrained
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.3156P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2906 reflections	$\Delta\rangle_{max} = 0.16$ e Å^{-3}
201 parameters	$\Delta\rangle_{min} = -0.21$ e Å^{-3}
0 restraints	Absolute structure: Refined as an inversion twin. Parsons' x = 0.494(4), Hooft's y = 0.493(6).
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.494 (18)

Computing details

Data collection: *APEX3*; cell refinement: *APEX3*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 1 deg., 7+1 runs, 1185 frames, 12/24 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Table 41: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **95b**

	X	*Y*	*z*	U_{iso}*/U_{eq}
N1	0.54193 (19)	0.53431 (12)	0.63174 (10)	0.0194 (3)
C2	0.5608 (2)	0.64008 (14)	0.63238 (12)	0.0189 (3)
S2	0.45635 (5)	0.71659 (4)	0.70859 (3)	0.02434 (13)
C3	0.6721 (2)	0.68414 (14)	0.56273 (13)	0.0182 (4)
C4	0.7424 (2)	0.62327 (15)	0.49424 (13)	0.0209 (4)
H4	0.8090	0.6540	0.4463	0.025*
C4A	0.7179 (2)	0.51406 (15)	0.49309 (14)	0.0203 (4)
C5	0.7926 (2)	0.44925 (17)	0.42419 (14)	0.0265 (4)
H5	0.8610	0.4787	0.3763	0.032*
C6	0.7681 (3)	0.34436 (17)	0.42526 (17)	0.0312 (5)
H6	0.8193	0.3013	0.3787	0.037*
C7	0.6674 (3)	0.30152 (16)	0.49541 (16)	0.0305 (5)
H7	0.6493	0.2290	0.4955	0.037*
C8	0.5935 (2)	0.36219 (16)	0.56452 (15)	0.0259 (4)
H8	0.5267	0.3314	0.6124	0.031*
C8A	0.6176 (2)	0.47015 (15)	0.56388 (13)	0.0200 (4)
C9	0.4351 (2)	0.48490 (16)	0.70262 (15)	0.0279 (4)
H9A	0.3933	0.5373	0.7475	0.042*
H9B	0.4947	0.4326	0.7395	0.042*
H9C	0.3460	0.4518	0.6683	0.042*
C10	0.7087 (2)	0.79707 (15)	0.56565 (13)	0.0189 (4)
C11	0.6453 (2)	0.86193 (16)	0.49695 (14)	0.0239 (4)
H11	0.5786	0.8345	0.4472	0.029*
C12	0.6778 (3)	0.96916 (17)	0.49912 (15)	0.0275 (4)
H12	0.6289	1.0134	0.4526	0.033*
C13	0.7780 (2)	1.00991 (15)	0.56695 (16)	0.0261 (4)
H13	0.7983	1.0822	0.5677	0.031*
C13A	0.8523 (2)	0.94471 (15)	0.63651 (14)	0.0207 (4)
C14	0.9625 (2)	0.98431 (15)	0.70576 (15)	0.0281 (4)
H14	0.9849	1.0564	0.7068	0.034*
C15	1.0369 (3)	0.92073 (18)	0.77090 (15)	0.0317 (5)
H15	1.1113	0.9485	0.8162	0.038*
C16	1.0033 (2)	0.81342 (18)	0.77096 (15)	0.0298 (5)
H16	1.0558	0.7692	0.8160	0.036*
C17	0.8953 (2)	0.77328 (15)	0.70625 (14)	0.0228 (4)
H17	0.8719	0.7014	0.7081	0.027*
C17A	0.8178 (2)	0.83671 (14)	0.63654 (13)	0.0186 (4)

Table 42: Atomic displacement parameters (Å^2) for **95b**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0188 (7)	0.0209 (7)	0.0184 (7)	-0.0037 (7)	0.0009 (6)	0.0003 (6)
C2	0.0173 (8)	0.0227 (8)	0.0167 (7)	-0.0005 (7)	-0.0020 (7)	-0.0011 (7)
S2	0.0268 (2)	0.0235 (2)	0.0227 (2)	-0.00021 (19)	0.00702 (18)	-0.00368 (17)
C3	0.0166 (8)	0.0213 (9)	0.0166 (8)	-0.0023 (7)	-0.0027 (7)	0.0002 (7)
C4	0.0175 (9)	0.0271 (11)	0.0182 (8)	-0.0035 (7)	0.0015 (7)	0.0009 (8)
C4A	0.0177 (8)	0.0235 (10)	0.0197 (8)	-0.0001 (8)	-0.0034 (7)	-0.0026 (7)
C5	0.0230 (10)	0.0341 (11)	0.0224 (9)	0.0048 (8)	-0.0003 (8)	-0.0048 (8)
C6	0.0317 (11)	0.0318 (12)	0.0302 (10)	0.0129 (9)	-0.0064 (9)	-0.0099 (9)
C7	0.0394 (11)	0.0190 (10)	0.0332 (10)	0.0051 (8)	-0.0108 (9)	-0.0040 (8)
C8	0.0306 (10)	0.0226 (9)	0.0243 (9)	-0.0018 (8)	-0.0059 (8)	0.0021 (8)
C8A	0.0198 (8)	0.0215 (9)	0.0188 (8)	0.0001 (7)	-0.0061 (7)	-0.0022 (7)
C9	0.0305 (10)	0.0272 (9)	0.0259 (9)	-0.0080 (8)	0.0074 (9)	0.0020 (8)
C10	0.0162 (8)	0.0222 (9)	0.0183 (8)	-0.0008 (7)	0.0019 (7)	-0.0002 (7)
C11	0.0205 (9)	0.0300 (10)	0.0212 (9)	-0.0013 (8)	-0.0011 (7)	0.0028 (8)
C12	0.0267 (10)	0.0284 (11)	0.0275 (10)	0.0049 (9)	0.0031 (8)	0.0104 (9)
C13	0.0277 (10)	0.0183 (9)	0.0323 (10)	-0.0014 (8)	0.0078 (8)	0.0037 (8)
C13A	0.0181 (9)	0.0201 (9)	0.0241 (9)	-0.0022 (7)	0.0066 (7)	-0.0012 (7)
C14	0.0230 (9)	0.0276 (9)	0.0335 (10)	-0.0080 (8)	0.0061 (10)	-0.0069 (8)
C15	0.0238 (10)	0.0449 (12)	0.0264 (9)	-0.0093 (9)	-0.0037 (8)	-0.0085 (8)
C16	0.0252 (10)	0.0397 (12)	0.0246 (10)	0.0003 (8)	-0.0058 (8)	0.0019 (8)
C17	0.0229 (9)	0.0229 (9)	0.0226 (8)	-0.0006 (7)	-0.0013 (7)	0.0030 (8)
C17A	0.0154 (8)	0.0222 (9)	0.0182 (8)	-0.0002 (7)	0.0033 (7)	0.0003 (7)

Table 43: Bond lengths (Å) for **95b**

N1—C2	1.376 (2)	C9—H9B	0.9800
N1—C8A	1.399 (2)	C9—H9C	0.9800
N1—C9	1.467 (2)	C10—C11	1.369 (3)
C2—C3	1.451 (2)	C10—C17A	1.429 (3)
C2—S2	1.6839 (18)	C11—C12	1.413 (3)
C3—C4	1.360 (3)	C11—H11	0.9500
C3—C10	1.492 (3)	C12—C13	1.359 (3)
C4—C4A	1.427 (3)	C12—H12	0.9500
C4—H4	0.9500	C13—C13A	1.417 (3)
C4A—C8A	1.404 (3)	C13—H13	0.9500
C4A—C5	1.410 (3)	C13A—C14	1.420 (3)
C5—C6	1.371 (3)	C13A—C17A	1.426 (2)
C5—H5	0.9500	C14—C15	1.365 (3)
C6—C7	1.394 (3)	C14—H14	0.9500
C6—H6	0.9500	C15—C16	1.415 (3)
C7—C8	1.377 (3)	C15—H15	0.9500
C7—H7	0.9500	C16—C17	1.369 (3)
C8—C8A	1.410 (3)	C16—H16	0.9500
C8—H8	0.9500	C17—C17A	1.418 (3)
C9—H9A	0.9800	C17—H17	0.9500

Table 44: Bond angles (Å) for **95b**

C2—N1—C8A	122.80 (15)	N1—C9—H9C	109.5
C2—N1—C9	119.86 (15)	H9A—C9—H9C	109.5
C8A—N1—C9	117.32 (16)	H9B—C9—H9C	109.5
N1—C2—C3	117.33 (15)	C11—C10—C17A	119.81 (17)
N1—C2—S2	121.88 (14)	C11—C10—C3	120.08 (16)
C3—C2—S2	120.77 (14)	C17A—C10—C3	120.01 (16)
C4—C3—C2	120.39 (17)	C10—C11—C12	120.79 (19)
C4—C3—C10	119.75 (17)	C10—C11—H11	119.6
C2—C3—C10	119.86 (16)	C12—C11—H11	119.6
C3—C4—C4A	121.22 (17)	C13—C12—C11	120.88 (19)
C3—C4—H4	119.4	C13—C12—H12	119.6
C4A—C4—H4	119.4	C11—C12—H12	119.6
C8A—C4A—C5	119.29 (18)	C12—C13—C13A	120.11 (18)
C8A—C4A—C4	118.57 (17)	C12—C13—H13	119.9
C5—C4A—C4	122.13 (18)	C13A—C13—H13	119.9
C6—C5—C4A	120.9 (2)	C13—C13A—C14	121.43 (17)
C6—C5—H5	119.5	C13—C13A—C17A	119.59 (17)
C4A—C5—H5	119.5	C14—C13A—C17A	118.98 (18)
C5—C6—C7	119.37 (19)	C15—C14—C13A	121.17 (18)
C5—C6—H6	120.3	C15—C14—H14	119.4
C7—C6—H6	120.3	C13A—C14—H14	119.4
C8—C7—C6	121.37 (19)	C14—C15—C16	120.02 (19)
C8—C7—H7	119.3	C14—C15—H15	120.0
C6—C7—H7	119.3	C16—C15—H15	120.0
C7—C8—C8A	119.7 (2)	C17—C16—C15	120.14 (19)
C7—C8—H8	120.2	C17—C16—H16	119.9
C8A—C8—H8	120.2	C15—C16—H16	119.9
N1—C8A—C4A	119.45 (17)	C16—C17—C17A	121.38 (18)
N1—C8A—C8	121.23 (18)	C16—C17—H17	119.3
C4A—C8A—C8	119.32 (18)	C17A—C17—H17	119.3
N1—C9—H9A	109.5	C17—C17A—C13A	118.29 (17)
N1—C9—H9B	109.5	C17—C17A—C10	122.99 (17)
H9A—C9—H9B	109.5	C13A—C17A—C10	118.71 (17)

Table 45: Torsion angles (Å) for **95b**

C8A—N1—C2—C3	-3.9 (2)	C7—C8—C8A—C4A	-0.6 (3)
C9—N1—C2—C3	177.95 (16)	C4—C3—C10—C11	74.3 (2)
C8A—N1—C2—S2	174.66 (13)	C2—C3—C10—C11	-105.2 (2)
C9—N1—C2—S2	-3.5 (2)	C4—C3—C10—C17A	-101.9 (2)
N1—C2—C3—C4	6.0 (3)	C2—C3—C10—C17A	78.6 (2)
S2—C2—C3—C4	-172.57 (14)	C17A—C10—C11—C12	-4.3 (3)
N1—C2—C3—C10	-174.57 (15)	C3—C10—C11—C12	179.50 (18)
S2—C2—C3—C10	6.9 (2)	C10—C11—C12—C13	2.8 (3)
C2—C3—C4—C4A	-4.5 (3)	C11—C12—C13—C13A	0.3 (3)
C10—C3—C4—C4A	176.06 (16)	C12—C13—C13A—C14	177.44 (18)
C3—C4—C4A—C8A	0.7 (3)	C12—C13—C13A—C17A	-1.7 (3)

Table 45 (continued).

C3—C4—C4A—C5	-178.44 (18)	C13—C13A—C14—C15	-178.24 (18)
C8A—C4A—C5—C6	0.3 (3)	C17A—C13A—C14—C15	0.9 (3)
C4—C4A—C5—C6	179.4 (2)	C13A—C14—C15—C16	-0.7 (3)
C4A—C5—C6—C7	0.2 (3)	C14—C15—C16—C17	-0.5 (3)
C5—C6—C7—C8	-0.9 (3)	C15—C16—C17—C17A	1.5 (3)
C6—C7—C8—C8A	1.1 (3)	C16—C17—C17A—C13A	-1.3 (3)
C2—N1—C8A—C4A	0.3 (3)	C16—C17—C17A—C10	177.72 (18)
C9—N1—C8A—C4A	178.48 (16)	C13—C13A—C17A—C17	179.27 (17)
C2—N1—C8A—C8	-179.03 (17)	C14—C13A—C17A—C17	0.1 (3)
C9—N1—C8A—C8	-0.8 (3)	C13—C13A—C17A—C10	0.2 (3)
C5—C4A—C8A—N1	-179.36 (16)	C14—C13A—C17A—C10	-178.99 (16)
C4—C4A—C8A—N1	1.4 (3)	C11—C10—C17A—C17	-176.23 (17)
C5—C4A—C8A—C8	-0.1 (3)	C3—C10—C17A—C17	0.0 (3)
C4—C4A—C8A—C8	-179.26 (18)	C11—C10—C17A—C13A	2.8 (3)
C7—C8—C8A—N1	178.70 (18)	C3—C10—C17A—C13A	179.01 (16)

Table 46: Hydrogen-bond geometry (Å, º) for **95b**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···S2^{i}	0.95	2.88	3.664 (2)	141
C9—H9*B*···S2^{i}	0.98	2.91	3.787 (2)	149

Symmetry code: (i) -*x*+1, *y*-1/2, -*z*+3/2.

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

Crystal structure determination of 1-methyl-3-(phenanthren-9-yl)quinoline-2(1H)-selenone 96c

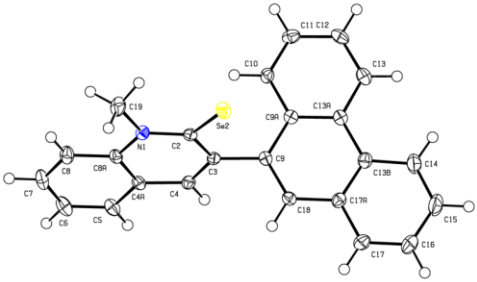


Figure 41: X-ray structure of molecules **96c**

Table 47: Crystallography data for **96b**

$C_{24}H_{17}NSe$	$F(000)$ = 808
M_r = 398.34	D_x = 1.504 Mg m^{-3}
Monoclinic, $P2_1/c$ *(no.14)*	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 6.1638 (2) Å	Cell parameters from 9894 reflections
b = 19.9050 (6) Å	θ = 3.8–72.1°
c = 14.3978 (4) Å	μ = 2.92 mm^{-1}
β = 95.257 (1)°	T = 123 K
V = 1759.04 (9) Å^3	Plates, red
Z = 4	0.22 × 0.06 × 0.02 mm

Table 48: Data collection for **96c**

Bruker D8 VENTURE diffractometer with Photon100 detector	3473 independent reflections
Radiation source: INCOATEC microfocus sealed tube	3138 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	R_{int} = 0.033
rotation in ϕ and ω, 1°, shutterless scans	θ_{max} = 72.1°, θ_{min} = 3.8°
Absorption correction: multi-scan *SADABS* (Sheldrick, 2014) T_{min} = 0.754, T_{max} = 0.929	h = -7→7 k = -24→23
16462 measured reflections	l = -17→17

Table 49: Refinement for **96c**

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 1.9833P]$ where $P = (F_o^2 + 2F_c^2)/3$
3473 reflections	$(\Delta/\sigma)_{max} = 0.001$
236 parameters	$\Delta\rangle_{max} = 0.44$ e Å^{-3}
0 restraints	$\Delta\rangle_{min} = -0.37$ e Å^{-3}

Computing details

Data collection: *APEX3*; cell refinement: *APEX3*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF*.

Special details

Experimental. dx = 40 mm, 1 deg., 11+1 runs, 1597 frames, 15/30 sec./frame

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 50: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) **96c**

	X	*Y*	*Z*	U_{iso}*/U_{eq}
N1	0.2999 (3)	0.20495 (9)	0.41496 (12)	0.0156 (4)
C2	0.3165 (3)	0.18911 (11)	0.50788 (14)	0.0146 (4)
Se2	0.51438 (4)	0.23139 (2)	0.59153 (2)	0.02069 (9)
C3	0.1657 (3)	0.14002 (10)	0.53897 (14)	0.0145 (4)
C4	-0.0008 (3)	0.11758 (11)	0.47928 (14)	0.0165 (4)
H4	-0.1042	0.0876	0.5016	0.020*
C4A	-0.0254 (3)	0.13768 (11)	0.38377 (15)	0.0163 (4)
C5	-0.1966 (4)	0.11424 (12)	0.32095 (16)	0.0218 (5)
H5	-0.3025	0.0846	0.3422	0.026*
C6	-0.2122 (4)	0.13388 (13)	0.22876 (17)	0.0265 (5)
H6	-0.3297	0.1186	0.1867	0.032*
C7	-0.0544 (4)	0.17619 (12)	0.19792 (15)	0.0248 (5)
H7	-0.0645	0.1891	0.1341	0.030*
C8	0.1157 (4)	0.19985 (12)	0.25712 (15)	0.0216 (5)
H8	0.2214	0.2288	0.2344	0.026*
C8A	0.1326 (3)	0.18092 (11)	0.35172 (14)	0.0154 (4)
C9	0.1876 (3)	0.11715 (11)	0.63800 (14)	0.0144 (4)
C9A	0.3614 (3)	0.07213 (11)	0.67230 (14)	0.0157 (4)
C10	0.5122 (3)	0.04663 (11)	0.61233 (15)	0.0181 (4)
H10	0.4991	0.0594	0.5485	0.022*
C11	0.6755 (4)	0.00412 (12)	0.64458 (16)	0.0221 (5)
H11	0.7746	-0.0124	0.6032	0.027*
C12	0.6977 (4)	-0.01526 (12)	0.73865 (17)	0.0225 (5)
H12	0.8124	-0.0445	0.7612	0.027*
C13	0.5530 (4)	0.00821 (12)	0.79813 (16)	0.0211 (5)
H13	0.5691	-0.0053	0.8617	0.025*
C13A	0.3809 (3)	0.05192 (11)	0.76728 (15)	0.0167 (4)
C13B	0.2230 (4)	0.07635 (11)	0.82884 (15)	0.0187 (4)
C14	0.2339 (5)	0.06093 (14)	0.92483 (17)	0.0311 (6)
H14	0.3483	0.0331	0.9517	0.037*
C15	0.0810 (5)	0.08561 (16)	0.98031 (17)	0.0372 (7)
H15	0.0918	0.0748	1.0448	0.045*
C16	-0.0891 (5)	0.12626 (15)	0.94260 (17)	0.0313 (6)
H16	-0.1937	0.1430	0.9812	0.038*
C17	-0.1044 (4)	0.14185 (13)	0.84974 (16)	0.0240 (5)
H17	-0.2209	0.1693	0.8240	0.029*
C17A	0.0512 (4)	0.11755 (11)	0.79149 (15)	0.0180 (4)
C18	0.0360 (3)	0.13640 (11)	0.69531 (14)	0.0164 (4)
H18	-0.0836	0.1631	0.6708	0.020*
C19	0.4589 (4)	0.25181 (13)	0.38071 (17)	0.0248 (5)
H19A	0.3983	0.2974	0.3787	0.037*
H19B	0.4909	0.2384	0.3179	0.037*
H19C	0.5933	0.2509	0.4227	0.037*

Table 51: Atomic displacement parameters (Å^2) **96c**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0172 (8)	0.0132 (9)	0.0165 (8)	-0.0008 (7)	0.0026 (7)	0.0010 (7)
C2	0.0154 (9)	0.0120 (10)	0.0166 (9)	0.0029 (8)	0.0021 (7)	-0.0006 (8)
Se2	0.02056 (14)	0.02260 (15)	0.01821 (14)	-0.00432 (10)	-0.00207 (9)	-0.00020 (9)
C3	0.0158 (9)	0.0129 (10)	0.0150 (10)	0.0032 (8)	0.0028 (8)	-0.0005 (8)
C4	0.0159 (10)	0.0162 (11)	0.0179 (10)	-0.0001 (8)	0.0036 (8)	0.0030 (8)
C4A	0.0179 (10)	0.0131 (10)	0.0175 (10)	0.0028 (8)	-0.0008 (8)	0.0014 (8)
C5	0.0226 (11)	0.0188 (11)	0.0230 (11)	0.0001 (9)	-0.0033 (9)	0.0036 (9)
C6	0.0300 (12)	0.0247 (13)	0.0226 (11)	0.0010 (10)	-0.0099 (10)	-0.0004 (9)
C7	0.0370 (13)	0.0213 (12)	0.0150 (10)	0.0045 (10)	-0.0042 (9)	0.0021 (8)
C8	0.0299 (12)	0.0162 (11)	0.0187 (10)	0.0014 (10)	0.0024 (9)	0.0039 (8)
C8A	0.0189 (10)	0.0116 (10)	0.0155 (10)	0.0030 (8)	0.0004 (8)	0.0009 (7)
C9	0.0151 (9)	0.0128 (10)	0.0150 (9)	-0.0024 (8)	-0.0006 (8)	0.0000 (8)
C9A	0.0160 (10)	0.0133 (10)	0.0176 (10)	-0.0010 (8)	0.0009 (8)	-0.0003 (8)
C10	0.0183 (10)	0.0189 (11)	0.0174 (10)	-0.0028 (9)	0.0029 (8)	0.0041 (8)
C11	0.0204 (11)	0.0187 (11)	0.0284 (12)	0.0029 (9)	0.0081 (9)	0.0001 (9)
C12	0.0201 (11)	0.0167 (11)	0.0297 (12)	0.0046 (9)	-0.0031 (9)	0.0035 (9)
C13	0.0242 (11)	0.0174 (11)	0.0209 (11)	0.0005 (9)	-0.0026 (9)	0.0017 (8)
C13A	0.0186 (10)	0.0141 (10)	0.0169 (10)	-0.0012 (9)	-0.0008 (8)	-0.0010 (8)
C13B	0.0222 (11)	0.0175 (11)	0.0165 (10)	-0.0003 (9)	0.0019 (8)	-0.0016 (8)
C14	0.0409 (15)	0.0352 (15)	0.0173 (11)	0.0129 (12)	0.0024 (10)	0.0033 (10)
C15	0.0507 (17)	0.0451 (17)	0.0167 (11)	0.0128 (14)	0.0087 (11)	0.0026 (11)
C16	0.0368 (14)	0.0389 (15)	0.0194 (12)	0.0068 (12)	0.0089 (10)	-0.0053 (10)
C17	0.0244 (11)	0.0267 (13)	0.0216 (11)	0.0046 (10)	0.0053 (9)	-0.0046 (9)
C17A	0.0199 (10)	0.0185 (11)	0.0158 (10)	-0.0008 (9)	0.0021 (8)	-0.0032 (8)
C18	0.0158 (10)	0.0162 (11)	0.0167 (10)	0.0007 (8)	-0.0005 (8)	-0.0008 (8)
C19	0.0263 (12)	0.0260 (12)	0.0222 (11)	-0.0105 (10)	0.0032 (9)	0.0063 (9)

Table 52: Bond lengths (Å) for **96c**

N1—C2	1.369 (3)	C10—H10	0.9500
N1—C8A	1.396 (3)	C11—C12	1.403 (3)
N1—C19	1.470 (3)	C11—H11	0.9500
C2—C3	1.447 (3)	C12—C13	1.374 (3)
C2—Se2	1.838 (2)	C12—H12	0.9500
C3—C4	1.353 (3)	C13—C13A	1.412 (3)
C3—C9	1.491 (3)	C13—H13	0.9500
C4—C4A	1.427 (3)	C13A—C13B	1.458 (3)
C4—H4	0.9500	C13B—C17A	1.407 (3)
C4A—C5	1.405 (3)	C13B—C14	1.411 (3)
C4A—C8A	1.409 (3)	C14—C15	1.381 (4)
C5—C6	1.379 (3)	C14—H14	0.9500
C5—H5	0.9500	C15—C16	1.394 (4)
C6—C7	1.390 (4)	C15—H15	0.9500
C6—H6	0.9500	C16—C17	1.367 (3)
C7—C8	1.373 (3)	C16—H16	0.9500

Table 52 (continued).

C7—H7	0.9500	C17—C17A	1.416 (3)
C8—C8A	1.408 (3)	C17—H17	0.9500
C8—H8	0.9500	C17A—C18	1.429 (3)
C9—C18	1.357 (3)	C18—H18	0.9500
C9—C9A	1.449 (3)	C19—H19A	0.9800
C9A—C10	1.419 (3)	C19—H19B	0.9800
C9A—C13A	1.420 (3)	C19—H19C	0.9800
C10—C11	1.364 (3)		

Table 53: Bond angles (º) for **96c**

C2—N1—C8A	122.87 (18)	C10—C11—C12	120.2 (2)
C2—N1—C19	118.80 (18)	C10—C11—H11	119.9
C8A—N1—C19	118.27 (18)	C12—C11—H11	119.9
N1—C2—C3	117.72 (18)	C13—C12—C11	119.8 (2)
N1—C2—Se2	121.35 (15)	C13—C12—H12	120.1
C3—C2—Se2	120.86 (15)	C11—C12—H12	120.1
C4—C3—C2	119.85 (19)	C12—C13—C13A	121.7 (2)
C4—C3—C9	120.23 (19)	C12—C13—H13	119.1
C2—C3—C9	119.83 (18)	C13A—C13—H13	119.1
C3—C4—C4A	121.8 (2)	C13—C13A—C9A	118.2 (2)
C3—C4—H4	119.1	C13—C13A—C13B	122.6 (2)
C4A—C4—H4	119.1	C9A—C13A—C13B	119.26 (19)
C5—C4A—C8A	119.5 (2)	C17A—C13B—C14	117.9 (2)
C5—C4A—C4	122.3 (2)	C17A—C13B—C13A	118.88 (19)
C8A—C4A—C4	118.13 (19)	C14—C13B—C13A	123.2 (2)
C6—C5—C4A	120.5 (2)	C15—C14—C13B	121.0 (2)
C6—C5—H5	119.8	C15—C14—H14	119.5
C4A—C5—H5	119.8	C13B—C14—H14	119.5
C5—C6—C7	119.4 (2)	C14—C15—C16	120.7 (2)
C5—C6—H6	120.3	C14—C15—H15	119.7
C7—C6—H6	120.3	C16—C15—H15	119.7
C8—C7—C6	121.8 (2)	C17—C16—C15	119.7 (2)
C8—C7—H7	119.1	C17—C16—H16	120.2
C6—C7—H7	119.1	C15—C16—H16	120.2
C7—C8—C8A	119.6 (2)	C16—C17—C17A	120.8 (2)
C7—C8—H8	120.2	C16—C17—H17	119.6
C8A—C8—H8	120.2	C17A—C17—H17	119.6
N1—C8A—C8	121.6 (2)	C13B—C17A—C17	120.0 (2)
N1—C8A—C4A	119.15 (18)	C13B—C17A—C18	120.24 (19)
C8—C8A—C4A	119.2 (2)	C17—C17A—C18	119.8 (2)
C18—C9—C9A	119.77 (19)	C9—C18—C17A	121.8 (2)
C18—C9—C3	119.22 (19)	C9—C18—H18	119.1
C9A—C9—C3	120.94 (18)	C17A—C18—H18	119.1
C10—C9A—C13A	118.85 (19)	N1—C19—H19A	109.5

Table 53 (continued).

C10—C9A—C9	121.27 (19)	N1—C19—H19B	109.5
C13A—C9A—C9	119.87 (19)	H19A—C19—H19B	109.5
C11—C10—C9A	121.3 (2)	N1—C19—H19C	109.5
C11—C10—H10	119.4	H19A—C19—H19C	109.5
C9A—C10—H10	119.4	H19B—C19—H19C	109.5

Table 54: Torsion angles (º) for **96c**

C8A—N1—C2—C3	6.4 (3)	C18—C9—C9A—C13A	-4.2 (3)
C19—N1—C2—C3	-176.61 (19)	C3—C9—C9A—C13A	179.00 (19)
C8A—N1—C2—Se2	-170.86 (15)	C13A—C9A—C10—C11	-0.8 (3)
C19—N1—C2—Se2	6.2 (3)	C9—C9A—C10—C11	-179.8 (2)
N1—C2—C3—C4	-7.9 (3)	C9A—C10—C11—C12	-0.1 (4)
Se2—C2—C3—C4	169.32 (16)	C10—C11—C12—C13	0.6 (4)
N1—C2—C3—C9	175.36 (18)	C11—C12—C13—C13A	-0.2 (4)
Se2—C2—C3—C9	-7.4 (3)	C12—C13—C13A—C9A	-0.8 (3)
C2—C3—C4—C4A	4.1 (3)	C12—C13—C13A—C13B	178.8 (2)
C9—C3—C4—C4A	-179.17 (19)	C10—C9A—C13A—C13	1.3 (3)
C3—C4—C4A—C5	179.4 (2)	C9—C9A—C13A—C13	-179.8 (2)
C3—C4—C4A—C8A	1.4 (3)	C10—C9A—C13A—C13B	-178.3 (2)
C8A—C4A—C5—C6	-0.8 (3)	C9—C9A—C13A—C13B	0.7 (3)
C4—C4A—C5—C6	-178.8 (2)	C13—C13A—C13B—C17A	-177.4 (2)
C4A—C5—C6—C7	1.2 (4)	C9A—C13A—C13B—C17A	2.1 (3)
C5—C6—C7—C8	-0.9 (4)	C13—C13A—C13B—C14	2.9 (4)
C6—C7—C8—C8A	0.2 (4)	C9A—C13A—C13B—C14	-177.6 (2)
C2—N1—C8A—C8	177.9 (2)	C17A—C13B—C14—C15	-0.1 (4)
C19—N1—C8A—C8	0.8 (3)	C13A—C13B—C14—C15	179.7 (3)
C2—N1—C8A—C4A	-0.9 (3)	C13B—C14—C15—C16	0.3 (5)
C19—N1—C8A—C4A	-178.0 (2)	C14—C15—C16—C17	0.0 (5)
C7—C8—C8A—N1	-178.5 (2)	C15—C16—C17—C17A	-0.4 (4)
C7—C8—C8A—C4A	0.3 (3)	C14—C13B—C17A—C17	-0.3 (3)
C5—C4A—C8A—N1	178.8 (2)	C13A—C13B—C17A—C17	179.9 (2)
C4—C4A—C8A—N1	-3.1 (3)	C14—C13B—C17A—C18	178.1 (2)
C5—C4A—C8A—C8	0.0 (3)	C13A—C13B—C17A—C18	-1.6 (3)
C4—C4A—C8A—C8	178.1 (2)	C16—C17—C17A—C13B	0.6 (4)
C4—C3—C9—C18	-67.3 (3)	C16—C17—C17A—C18	-177.9 (2)
C2—C3—C9—C18	109.4 (2)	C9A—C9—C18—C17A	4.8 (3)
C4—C3—C9—C9A	109.6 (2)	C3—C9—C18—C17A	-178.3 (2)
C2—C3—C9—C9A	-73.7 (3)	C13B—C17A—C18—C9	-1.9 (3)
C18—C9—C9A—C10	174.8 (2)	C17—C17A—C18—C9	176.6 (2)
C3—C9—C9A—C10	-2.0 (3)		

Table 55: Hydrogen-bond geometry (Å, º) for **96c**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···Se2^{i}	0.95	2.97	3.830 (2)	152
C19—H19*C*···Se2	0.98	2.55	3.050 (2)	112

Symmetry code: (i) *x*, -*y*+1/2, *z*-1/2.

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

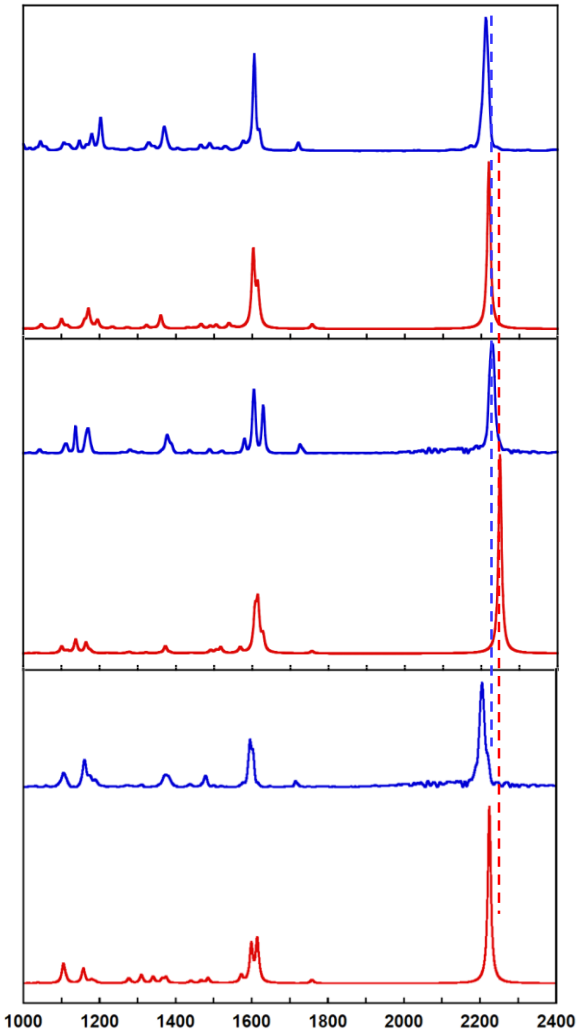


Figure 42: Experimental (red lines) and b3lyp/6-311g(d,p) (blue lines) Raman spectra of cations **42b** (2-yl, bottom panel), **42c** (4-yl, upper panel) and **42a** (3-yl, middle panel)

5.6 Additional results of calculations

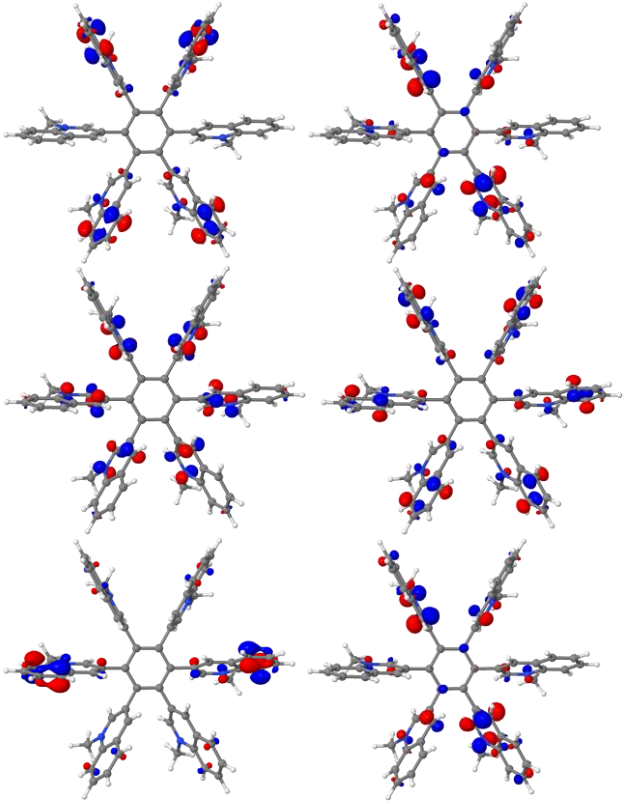
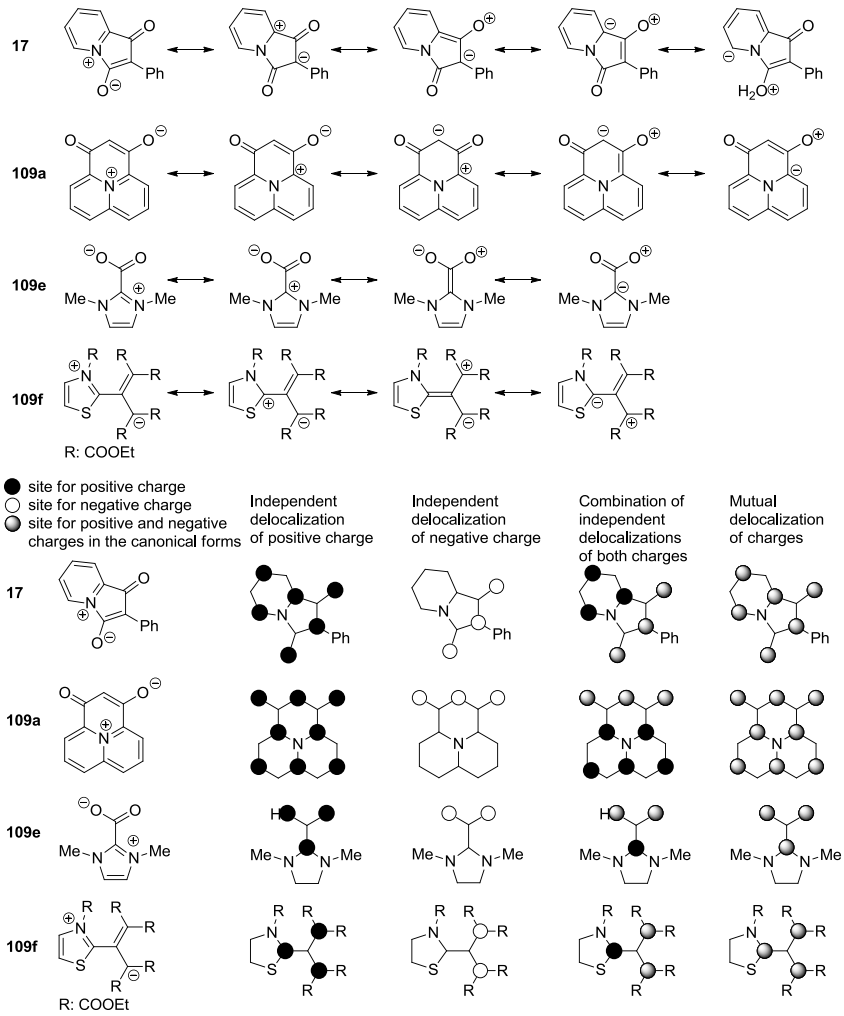


Figure 43: HOMO-1/LUMO+1 (above), HOMO/LUMO (midle) and HOMO-2/LUMO+2 (below) profiles of **88 A** rotamer



Scheme 117: Delocalization of charges in RAMSDEN's PCCMBs

Table 56: Calculations of UV/Vis spectra of **77a**, **c**, **d**

TDDFT Excitation Energies (77a)

State	Hartree	eV	Kcal/mol	cm^{-1}	nm	Osc. str.
1A	0.1110904178	3.0229	69.7103	24381.53	410.15	2.8015063
1A	0.1260683297	3.4305	79.1091	27668.80	361.42	0.0000144
1A	0.1264030445	3.4396	79.3191	27742.26	360.46	0.0396871
1A	0.1328765680	3.6158	83.3813	29163.04	342.90	0.0000087
1A	0.1440802765	3.9206	90.4118	31621.97	316.24	0.0175686
1A	0.1457088101	3.9649	91.4337	31979.39	312.70	0.0000163
1A	0.1514238625	4.1205	95.0199	33233.70	300.90	0.0229343
1A	0.1523342540	4.1452	95.5912	33433.50	299.10	0.0000006
1A	0.1537446396	4.1836	96.4762	33743.05	296.36	0.0003094
1A	0.1546146524	4.2073	97.0222	33933.99	294.69	0.0000786
1A	0.1623536744	4.4179	101.8785	35632.51	280.64	0.0733893
1A	0.1642290490	4.4689	103.0553	36044.11	277.44	0.0342779

TDDFT Excitation Energies (77c)

State	Hartree	eV	Kcal/mol	cm^{-1}	nm	Osc. str.
1A	0.1022293383	2.7818	64.1499	22436.75	445.70	0.6351776
1A	0.1046960172	2.8489	65.6978	22978.12	435.20	0.0000609
1A	0.1297230591	3.5299	81.4025	28470.92	351.24	2.1595992
1A	0.1394100779	3.7935	87.4812	30596.98	326.83	0.0001424
1A	0.1413161889	3.8454	88.6773	31015.32	322.42	0.0004135
1A	0.1416798074	3.8553	88.9054	31095.12	321.59	0.0943361
1A	0.1442167282	3.9243	90.4974	31651.91	315.94	0.0000000
1A	0.1490327703	4.0554	93.5195	32708.91	305.73	0.0000071
1A	0.1517235192	4.1286	95.2080	33299.46	300.31	0.2287821
1A	0.1523649573	4.1461	95.6105	33440.24	299.04	0.0347488
1A	0.1526558399	4.1540	95.7930	33504.08	298.47	0.0002948
1A	0.1586508046	4.3171	99.5549	34819.83	287.19	0.0000008

TDDFT Excitation Energies (77d)

State	Hartree	eV	Kcal/mol	cm^{-1}	nm	Osc. str.
1A	0.1086122916	2.9555	68.1553	23837.64	419.50	1.3625777
1A	0.1161147913	3.1596	72.8631	25484.25	392.40	0.9455724
1A	0.1308280619	3.5600	82.0959	28713.44	348.27	0.0233437
1A	0.1415186827	3.8509	88.8043	31059.76	321.96	0.2107438
1A	0.1443947207	3.9292	90.6091	31690.98	315.55	0.0135363
1A	0.1447430654	3.9387	90.8277	31767.43	314.79	0.3278415
1A	0.1481772243	4.0321	92.9826	32521.14	307.49	0.0053947
1A	0.1512971944	4.1170	94.9404	33205.90	301.15	0.0037865
1A	0.1524082355	4.1472	95.6376	33449.74	298.96	0.0012063
1A	0.1540515369	4.1920	96.6688	33810.40	295.77	0.0000344
1A	0.1551518170	4.2219	97.3592	34051.89	293.67	0.0000316
1A	0.1559969659	4.2449	97.8896	34237.38	292.08	0.3867628

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